

# Adhesives and Sealants

## Technology, Applications and Markets

David J. Dunn

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TECHNOLOGY





# **Adhesives and Sealants – Technology, Applications and Markets**

## **A Rapra Market Report**

*by*

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**March 2003**



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# **1 Introduction**

## **1.1 The World of Adhesives and Sealants**

Adhesives and sealants is a \$20 billion+ global industry that serves many applications and end-markets. Its value chain ranges from basic petrochemical and mineral products all the way to end-users who may be aerospace companies, industrial manufacturers or consumers.

The vast majority of items of commerce use adhesives and sealants as a basic component in their manufacture or in their packaging.

Adhesives are performance products, purchased primarily for what they do rather than their chemical basis, but range from commodity items, like starches used in box manufacturing and styrene-butadiene latices used in carpet manufacturing, to speciality items such as cyanoacrylate adhesives used in surgery or exotic aerospace sealants. Prices of these items range from less than US\$0.5 /kilo for commodity adhesives to as much as US\$2000/kilo for highly specialised items.

Adhesives may come from animal or plant origins or be synthetic products derived from petroleum products.

The oldest adhesives are polysaccharides and proteins, which are high molecular weight natural polymers derived from plants and animals. Animal, blood, hide, casein, starch, soybean, dextrin, and cellulosic adhesives are all derived from the natural polymers found in these sources. They have been used as adhesives for centuries and are still in use today, although most have been replaced by adhesives made with synthetic polymers.

## **1.2 Scope**

This report covers the global technology and markets for liquid, solid and film adhesives and sealants. Other methods of sealing such as pre-formed seals and gaskets made from elastomers and plastics are not covered. The report shows the basic chemistry of the manufacturing, formulating and curing of adhesives and sealants including recent developments. There is no coverage of the basic science of adhesion, which is a subject in its own right, engineering with adhesives, or application and dispensing equipment.

## **1.3 Geographical Focus**

The report focuses mainly on two important and inter-related end-user markets: Western Europe and North America, and also covers emerging growth markets in the Far East.

## **1.4 Methodology**

This report forms one of a series written and produced over the last several years for the Industry Analysis Unit at Rapra Technology Limited. These reports cover various aspects of polymer materials and/or their application in specified end products. Some of the unit's reports have been compiled specifically for a single client or a limited number of sponsoring clients, but others, like the present one, are available for sale.

The information presented here is based mainly on an analysis of the most recent technical and commercial literature including, but not limited to, the Rapra Polymer Library (Abstracts) database. The database is acknowledged to be the world's leading source of industrially relevant published information on the plastics industry. Other information comes from recent conferences, seminars, trade fairs, interviews and company web sites.

## 1.5 Units

SI units are used throughout with demand or production figures being quoted in metric tons or kilos. For properties of adhesives, SI units are used with imperial units in parentheses for the convenience of US readers.

To convert	Into	Multiply by
kg	lb	2.2
metric tons	lb	2200
p.s.i	MPa	$6.895 \times 10^{-3}$
MPa	p.s.i.	143.88
N/cm	pli	0.57
pli	N/cm	1.751
cP	mPa.s	1
Poise	Pa.s	1

The currency in use is US dollars unless otherwise stated.

## 1.6 Authorship

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## 2 Executive Summary

### 2.1 Overview

Adhesives and sealants is a 20 million ton global industry with a sales value of over \$20 billion and serves many applications and end-markets. Its value chain ranges from basic petrochemical and mineral products all the way to end-users who may be aerospace companies, industrial manufacturers or consumers (Figure 2.1).

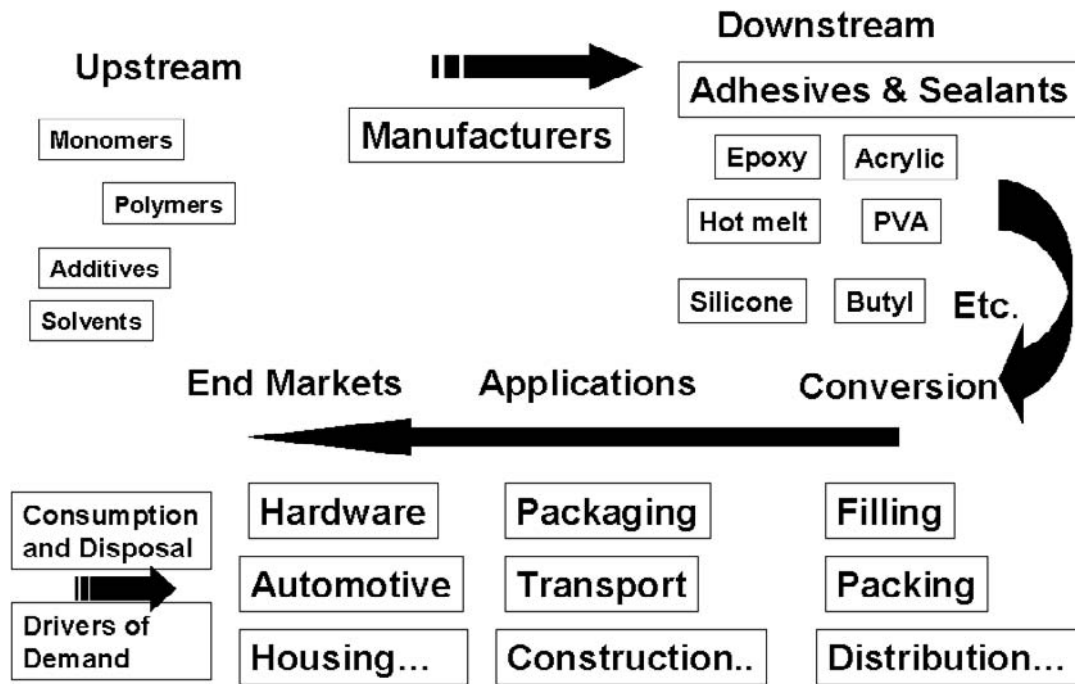


Figure 2.1 Overview of the adhesives and sealants value chain

Adhesives are primarily designed to hold or stick things together, whereas the function of sealants is to prevent the leakage of fluids or gases, or seal against the ingress of atmospheric components into an assembly.

Although the functions of adhesives and sealants are nominally different, their technology bases are similar.

Market forces have caused adhesives to evolve into three general categories:

- Commodity adhesives
- General purpose adhesives
- Speciality adhesives

Commodity adhesives are those whose raw materials' prices fluctuate according to supply and demand, where supply exceeds demand or where there has been a concentration of the customer base. Commodity adhesives are:

- Formaldehyde resins
- Starch and dextrin adhesives
- Styrene-butadiene latex for carpet manufacture

General purpose adhesives are those where large volumes are sold but where there are still opportunities for product differentiation. General purpose adhesives include:

- Latex adhesives
- Hot melts
- Solvent based adhesives
- Pressure sensitive adhesives
- Inorganic adhesives

Speciality adhesives are often custom formulated for specific applications or sold in such low volumes that they demand high prices. Speciality adhesives include:

- Polyurethane
- Reactive hot melt polyurethanes
- Epoxies
- Cyanoacrylates
- Anaerobics
- Reactive acrylics
- UV adhesives

The largest applications for adhesives are commodity adhesives for binding of wood particles in the manufacturing of wood panels and the use of starch based adhesives for manufacturing corrugated and paperboard cartons. These applications consume over two-thirds of the adhesive volume globally but are sold typically for low prices from \$0.50 to \$1 per kg.

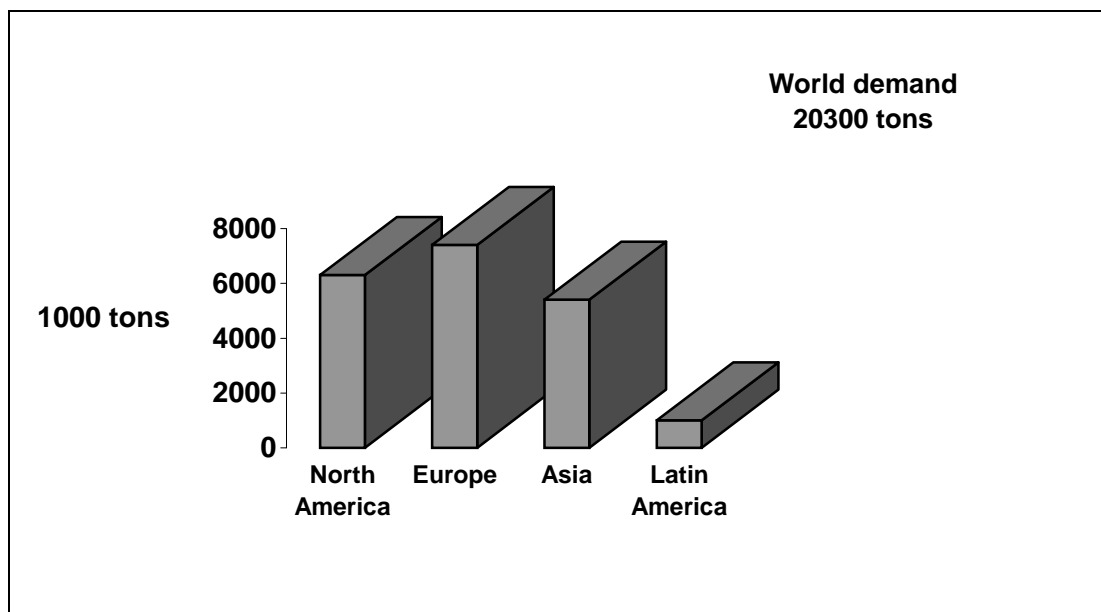
General purpose adhesives include hot melts, pressure sensitive adhesives (PSAs) and latex (emulsion) adhesives, categories that are experiencing significant growth because of their environmentally friendly nature.

Speciality adhesives comprise less than 5% of the volume but a much larger share of the value of the total adhesives market. Unless there is considerable investment in product differentiation, some speciality adhesives will become general purpose adhesives, where price may become the dominant purchasing factor.

The adhesives industry serves a wide range of market segments including:

Packaging and labelling	Construction
Textiles and carpets	Consumer
Product assembly	Transportation
Medical	Plumbing

When all types of adhesives are considered, Europe is the largest market for adhesives, followed closely by North America (Figure 2.2).



**Figure 2.2 Global consumption of adhesives by region, 2001**

The sealants industry is much smaller in volume than adhesives, comprising some 600,000 tons with a value of \$3.5 billion. Its main technologies include:

- RTV silicones
- polyurethanes
- latex
- polysulfide
- vinyl plastisol

Although marketed to several market segments, the major applications are in the construction industry. Europe and North America combined have around a 75% market share.

The adhesives and sealants industry has been changed significantly over the last few years by a series of mergers and acquisitions. Some of this has been aggressive global expansion by large companies and some caused by increasing consolidation in the customer base. However, the industry is still very fragmented with a few thousand suppliers worldwide. We will continue to see the industry giants acquiring smaller specialist or regional manufacturers to establish a market position or gain a specific technology.

A handful of large companies now hold a very large global market share. These leading companies are Henkel, Avery Dennison, H.B. Fuller, 3M, Bostik-Findley, National Starch, Sika and UPM-Kymmene, all with sales over \$1 billion. There are also several companies with sales of \$300 to 700 million.

Growth in adhesives and sealants will be influenced by increases in the global GDP and by the growth of the individual end-user market segments.

## **2.2 Market Drivers**

*Global market* – The overall market is global and very large and is spread across a wide range of both industrial and consumer markets.

*Regional expansion* – High growth is expected in China and Latin America.

*Growth in key segments* – There are high growth rates in several markets, e.g., the housing market, medical, packaging and automotive.

*Replacement of solvent-based systems* – Worldwide legislation on solvent emissions will create more opportunities for hot melt latex and other water-based systems to replace solvent based adhesives and sealants.

*100% solid systems* – technologies such as hot melts, reactive acrylics and UV systems will grow because of their safety and energy efficiency.

*Replacement of other fastening methods* – adhesives will continue to replace mechanical fastening systems due to better performance and overall lower costs.

*High performance sealants* – architects increasingly specify silicones and polyurethanes in place of preformed seals because of their ease of application, high performance and durability.

## **2.3 Market Restraints**

*Economic cycles* – certain market segments are in low growth or declining modes, e.g., the commercial aerospace industry and telecommunications and others are influenced strongly by macroeconomic cycles, e.g., the automotive and construction industry.

*Automotive and carpet industries* – customer consolidation has led to intense pricing pressures on suppliers.

*Non-woven industry* – replacement of adhesives by thermal bonding and hydro entanglement technology.

*Raw material prices* – recent increases in raw materials prices are a major concern, particularly to suppliers in price sensitive markets like wood resins and carpet adhesives.

## **2.4 Market Prospects**

The overall prospects for adhesives and sealants remain positive. These seemingly products of low significance are in fact critical components of modern society, affecting the quality and safety of our food, the performance of our cars and aeroplanes and the assembly of literally millions of industrial and household items. Adhesives and sealants are usually an insignificant factor in the overall cost of a product, but can have dramatic effects on the productivity of an operation and the quality of a product.

The winners in this industry will not be those that only try to reduce the costs of adhesives or sealants, internal competition in the adhesives industry will take care of that, but those who continually innovate in all aspects of their operations and strive to find newer, better and faster products that will dramatically influence the cost-effectiveness of customers' operations.

## **3 Technology**

### **3.1 Introduction to Adhesives**

Adhesives are designed to hold materials together by surface attachment, often as alternatives to mechanical fastening systems. They are often called ‘glues’ by the do-it-yourselfer or craftsman but engineers prefer the term ‘adhesives’. Adhesives come in several forms: thin liquids, thick pastes, films, powders, pre-applied on tapes, or solids that must be melted. Adhesives can be designed with a wide range of strengths, all the way from weak temporary adhesives for holding papers in place to high strength structural systems that bond cars and aeroplanes. In many industries, adhesives compete with mechanical fastening systems such as nuts and bolts, rivets or welding, and soldering.

Adhesives offer several benefits for the joining of materials:

- They distribute loads across the entire joint area.
- They show excellent fatigue properties.
- They attenuate mechanical vibrations and sound.
- Adhesives often fulfill a dual role of acting as both adhesives and also sealing a joint against ingress of water or other fluids.
- Because of their low electrical conductivity, adhesives significantly reduce galvanic corrosion between dissimilar metals.
- They give unobtrusive bond lines.
- Adhesive assembly is often much faster and more cost-effective than mechanical methods.

### **3.2 Important Properties of Adhesives**

Important properties that must be considered when choosing an adhesive include:

- Rate of cure
- Gap filling capability
- Bonding dirty surfaces
- Tensile shear strength
- Peel strength
- Impact resistance
- Load bearing capability
- Heat and cold resistance
- Fluid resistance
- Weatherability
- Health and safety issues

#### **3.2.1 Rate of Cure**

The speed at which an adhesive provides handling strength and then proceeds to full cure is critically important in some industries. Consumers love instant adhesives for instant repairs. In an automotive or industrial assembly, fast curing means productivity and is usually essential. Fast curing is also important in maintenance operations in which a piece of equipment or a vehicle must be back in service as soon as possible. Some adhesives, like cyanoacrylates or hot melts, give handling strength in seconds, while others often require clamping to allow strength build up. In some applications, controlled rate of cure is particularly desirable. For example, reactive acrylic adhesives can be formulated to give an induction time where no polymerisation takes place and

allow assembly of large complex parts, followed by a rapid polymerisation to give quick handling strength.

### **3.2.2 Gap Filling Capability**

Although adhesives do not typically handle very large gaps as compared to sealants, the ability to fill gaps is a very important property of adhesives, particularly when they are used to bond uneven surfaces or parts with large manufacturing tolerances. Cyanoacrylate and anaerobic adhesives, which have the convenience of being one-component systems do have the distinct weakness that their polymerisations are initiated from the surface being bonded and lack of molecular diffusion as polymerisation proceeds prevents curing through large gaps. In order to improve this situation surface primers must be used, thus eliminating the very desirable one-component nature of the adhesives. Two-component systems like epoxies and polyurethanes have their components thoroughly mixed before application and can normally be used for very large gaps.

### **3.2.3 Bonding Dirty Surfaces**

Except in electronics or medical applications, adhesives are often expected to deal with surfaces that are contaminated with process oils, rust preventatives or mould release agents. The ability to deal with these contaminants without extensive surface cleaning is an important factor in determining the economic viability of an adhesive for a particular application. Mechanical fasteners do not have this limitation. Adhesives like reactive acrylics are particularly good at bonding to contaminated surfaces.

### **3.2.4 Tensile Shear Strength, Peel Strength, Impact Resistance**

These properties are inter-related and are often the key properties associated with a particular adhesive technology. They are not as important when bonding weak substrates like paper or wood, where the strength of adhesives usually vastly exceeds the strength of the substrate, but are critical in bonding metals or high strength plastics. Most adhesive bonds are designed to give tensile shear forces on the adhesive. The tensile shear strength is the strength of an adhesive bond when it is pulled apart, parallel to the bond line. Adhesive types like epoxies, cyanoacrylates, reactive acrylics and polyurethanes can often give tensile shear strengths of 20 to 35 MPa (3000-5000 psi).

Impact resistance is often a key requirement for components operating under dynamic stresses and is a characteristic associated with elastomeric adhesives or those toughened with elastomers.

Peel strength is a method of testing a bond of two flexible materials, or a flexible and a rigid material, whereby the flexible material is pulled from the mating surface at a 90° or 180° angle to the plane onto which it is adhered. This has traditionally been the mode in which structural adhesives are the weakest. Some adhesive bonds used in the automotive industry have frequently been augmented with rivets at their ends to prevent failure from peel forces. Some adhesives, like reactive acrylics and polyurethanes, have very good peel strengths associated with their elastomeric backbones. Others like anaerobics, cyanoacrylates and epoxies have intrinsically low peel strengths, although developments such as toughening with elastomers have improved their properties substantially.

### **3.2.5 Load Bearing Capability**

Adhesives used in structural applications, such as in the construction or automotive industry must have a high modulus (and, often, toughness), but must not creep under operating loads. Load bearing capability is associated with highly crosslinked thermoset systems and epoxies have been the material of choice for most applications involving metal bonding.



### **3.2.6 Heat and Cold Resistance**

Adhesives can be used at extremes of high and low temperatures. At low temperatures, adhesives become glassy and hard and tensile shear strengths are usually very high. However, impact resistance and peel strengths become very low, particularly if the toughening elastomers are cooled below their glass transition temperatures ( $T_g$ ). Adhesives designed for operating at low temperatures use monomers and polymers with glass transition temperatures way below room temperature.

High temperatures can cause a loss of strength of adhesives and ultimately degradation of the polymers. The most common properties measured are heat-strength and strength after heat ageing. Thermoplastic polymers such as polycyanoacrylates and hot melts soften and fail at temperatures close to their  $T_g$ s and can rarely be used above 85-90 °C, whilst highly crosslinked thermosets such as anaerobics and epoxies have very good hot-strengths and can retain tensile shear strength, often to around 200 °C.

Heat ageing of adhesive bonds ultimately measures the onset of degradation of the polymers and is indicative of the longevity of the bonds at elevated temperatures. The resistance of an adhesive to heat ageing is dependent on its molecular structure and the degree of crosslinking. Additives can often be added to adhesives to improve heat ageing. For very high temperatures, above 300 °C, inorganic adhesives must be used.

### **3.2.7 Fluid Resistance**

Most adhesives are not exposed continuously to fluids in the same way that sealants are, but resistance is sometimes important both during processing and in service. Typical examples are under-the-bonnet adhesives in automotive that are exposed to oils and gasoline vapours, and adhesives used to bond needles in pre-filled medical syringes, which have continuous exposure to water. Adhesives can fail in two ways when exposed to aggressive fluids, either an interfacial adhesive failure, or dissolving or softening of the organic matrix. Additives such as silane adhesion promoters have been shown to be very beneficial in preventing adhesive failures in systems like epoxies and acrylics that are exposed to water.

### **3.2.8 Weatherability**

Weatherability of adhesives is important in outdoor applications, although effects such as UV degradation are not as important as with sealants, because adhesives are usually protected by opaque substrates. The exception to this is adhesives for bonding glass where possible UV degradation must be taken into account. A good example is polyurethane adhesives for automotive windshield installation that are pigmented black to protect against UV. Testing of an outdoor adhesive joint against the combined effects of heat, cold, wind and rain is highly recommended.

### **3.2.9 Health and Safety Issues**

Over the last 30 years or so there has been a dramatic shift away from the use of organic solvents in adhesives because of flammability and toxicity concerns. Although total emissions from adhesives is quite low compared to that from the coatings industry, legislation is in place in most parts of the world to limit the use of solvents. This has led to a dramatic increase in the use of latex adhesives, hot melts and 100% solids adhesives. However, even some of these systems have toxicity concerns, notably the amine hardeners in epoxies and isocyanates in polyurethanes.

There are still some adhesives where the use of solvents is beneficial to performance. For example, polychloroprene adhesives are available in both solvent and latex form but the solvent versions still give the best overall performance for most applications.

### **3.3 Introduction to Sealants**

Sealing has been defined as ‘the art and science of preventing leaks’ [1].

A sealant is normally used either to prevent a fluid or gas from escaping from an assembly or to prevent the ingress of components of the atmosphere into the assembly.

The distinction between adhesives and sealants is not always very clear. Most sealants are adhesives but their primary function is to seal a joint with adhesion merely being one important property. Some systems are true adhesive-sealants and fulfill the dual role of bonding and sealing a joint. Although most sealants are highly viscous liquids, some, such as porosity sealants, can be very low viscosity ‘water-thin’ liquids. Liquid sealants are often an alternative to pre-formed seals and gaskets based on elastomers, plastics or composite materials.

### **3.4 Important Properties of Sealants**

There are usually several types of sealant available for a particular application. The product designer or architect has to be able to choose the most cost-effective sealant that will perform in the joint to be sealed and have the requisite durability for the expected lifetime of the product [2].

All sealants must fulfill three basic functions:

1. Fill the space to create a seal
2. Form an impervious barrier to fluid flow
3. Maintain the seal in the operating environment.

First, the sealant must flow and totally fill the space between the surfaces, and it is very important that it is able to conform to surface irregularities. Strong adhesion to the joint surfaces is also a necessary requirement for most sealant applications.

Second, the sealant must be totally impervious to fluid flow. Some older traditional sealing materials such as fibre sheet packings and cork are impermeable only when sufficiently compressed to close their inherent porosity. Most elastomers used in sealants are inherently impermeable to liquids, but care must be taken when gases or vapours are involved. For example, silicones are excellent sealants for liquid water but have high moisture vapour transmission rates.

Third, the sealant must maintain the seal throughout the life expectancy of the joint, often under severe operating and environmental conditions. Exterior sealants in buildings must be able to accommodate large changes in joint width from temperature cycling, often over 50% in compression and tension, and must withstand the effects of heat, rain and ultraviolet (UV) light.

Aircraft, automotive and industrial sealed assemblies are often exposed to severe movements caused by vibration, mechanical strain, and changes in temperature, pressure, and velocity. The sealants in these systems must also be inert to the chemical effects of sealed liquids, which can encompass a wide range of materials, including aqueous solutions, hydraulic fluids, gasoline, organic chemicals, motor oil, jet fuel, liquid oxygen, strong acids and alkalis. Aggressive liquids can cause the swelling, chemical degradation, and debonding of a sealant. Although a small amount of swelling can help to seal a joint, severe swelling is often the first symptom of the onset of chemical degradation.

Important properties that must be considered when choosing a sealant include:

- Rate of cure
- Depth of cure
- Shrinkage on curing

- Adhesion
- Hardness and flexibility
- Tensile strength
- Compressive strength and compression set
- Stress relaxation
- Creep
- Heat and cold resistance
- Fluid resistance
- Moisture and gas permeability
- UV resistance

### **3.4.1 Curing Properties**

#### **3.4.1.1 Rate of Cure**

The speed at which a sealant builds up strength and then proceeds to full cure is critically important in some industries. In the construction industry, for example, slow cures imply that joint movement will take place during curing, which can sometimes lead to failure. However, it is important that materials do not cure faster than can be handled in a production environment. Primers or two-component systems are used to increase the rates of cure.

#### **3.4.1.2 Depth of Cure**

Depth of cure is another important consideration for a sealant. One-component systems, such as silicones, urethanes, and polysulfides, which depend on the diffusion of atmospheric moisture into the sealant for curing, can take days or even weeks for deep section curing. Anaerobic sealants, whose cure is initiated from metal surfaces, will not cure through gaps greater than about 0.5 mm (0.02 in).

#### **3.4.1.3 Shrinkage on Curing**

Shrinkage upon curing is a critical factor for any sealing system. Excessive shrinkage can lead to voids in a joint and induce stress in the sealant. Low-shrinkage products are those that have very high or 100% solids contents, including urethanes, silicones, polysulfides, plastisols, high-solids butyls, and anaerobics. Medium-shrinkage systems include hot-melt or hot-applied products such as asphalts, coal tars, and polypropylenes. High-shrinkage systems are all solvent- or aqueous-base sealants in which shrinkage is due to evaporation of the carrier. Some automotive butyl sealants are formulated with blowing agents and actually expand during curing to fill all voids. Foamed hot-melt sealants also expand after application.

### **3.4.2 Physical Properties of Sealants**

The vast majority of sealed joints experience some movement during service, and some flexibility in a sealant is essential. The only truly rigid sealants are anaerobics, because they tend to unitise an assembled joint and prevent it from moving. However, this lack of flexibility is sometimes considered a weakness in these products.

The physical properties that are important for a sealant are identified next. They should be measured after initial complete curing and then monitored under accelerated ageing conditions.

#### **3.4.2.1 Hardness**

Hardness is measured by the amount of penetration of a durometer in the cured sealant. Most sealants have Shore A durometer readings of 15 to 70. A change in hardness upon ageing is an indication that further curing or degradation is taking place.

#### **3.4.2.2 Modulus of Elasticity**

This is the ratio of the force (stress) required to elongate (strain) a sealant. In general, low- or medium-modulus sealants are able to accommodate much greater joint movement without putting a large stress on either the sealant or the substrate surfaces. Tensile strength is needed to some degree to avoid cohesive failure under stress. High tensile strength is not necessary for most sealants, except in high-pressure fluid sealing applications.

#### **3.4.2.3 Compressive Strength and Compression Set**

Compressive strength and compression set are important parameters for sealing building and automotive joints, threaded fittings, and gasketing. Compressive strength is the maximum compressive stress that a material can withstand without breaking down or experiencing excessive extrusion.

Compression set is the inability of a sealant to re-expand to its original dimensions after being compressed. It is usually expressed as the percentage loss of original thickness of a specimen after compression. High compression set is usually caused by further curing or degradative crosslinking of the material and is very undesirable in a joint that can expand and contract. It is important, particularly for transportation and industrial sealants, that compression set be measured under actual conditions of use, for example, at high operating temperatures and in contact with the fluid to be sealed. In general, silicones and urethanes have the lowest compression sets, followed by polysulfides, butyls and acrylics, although large variations in quality exist among suppliers.

#### **3.4.2.4 Stress Relaxation**

This is a condition in which the stress decays as the strain (amount of elongation) remains constant. Some very low modulus sealants literally get pulled apart when held at quite low elongations.

#### **3.4.2.5 Creep**

Creep is the condition in which the strain (amount of elongation) increases as the stress remains constant. This property is very important for applications in which sealants must bear structural loads.

### **3.4.3 Thermal Properties of Sealants: Heat and Cold Resistance**

All elastomers of the type used in sealants get stiffer when cold and softer when hot. If a joint will experience low and high temperatures in service, test data should be generated to include cycling between the temperature extremes. The effect of heat ageing on sealant properties should always be measured, particularly if continuous or intermittent exposure to high temperatures is expected. High temperatures usually soften a material initially and are often followed by degradation and embrittlement. Acrylics and butyls are not normally recommended for use at temperatures above 80 °C (175 °F). Urethanes and polysulfides are normally used below 100 °C (212 °F), but special high-temperature versions to 150 °C (300 °F) exist. Normal continuous service temperature for anaerobics is 150 °C (300 °F), but 200 °C (390 °F) versions are available. Most silicones are recommended for use to 200 °C (390 °F), but special reversion-stable versions have been tested and used successfully to over 300 °C (570 °F) in automotive gasketing applications.

### **3.4.4 Chemical Properties of Sealants**

Consideration must be given to the environment the sealant is likely to experience. For most aerospace, automotive and industrial sealants, suppliers have generated compatibility charts for many different industrial fluids and chemicals. In general, highly crosslinked thermoset plastics like anaerobics have extremely good resistance to most chemicals. It should be borne in mind that,

compared to the length of the seal (potential leak path), the area of exposure of the sealant to a chemical is very small in applications such as thread or porosity sealing. Thus, some degradation can be tolerated without loss of the seal. Elastomers are not as highly crosslinked as anaerobics and can often be severely swollen, debonded and degraded by certain fluids.

It should be noted that resistance to one chemical does not necessarily transfer to nominally similar chemicals. For example, silicones can be formulated to be quite resistant to hot oils, but are highly swollen by gasoline. Water and moisture resistance is often very important in sealant applications in which weather exposure or water immersion is expected, for example, in construction, glazing, marine, electronics and electrical applications. Urethanes are preferred for below-waterline applications in marine markets, whereas silicones are not recommended even though they are commonly used as seals in aquariums. Both silicones and urethanes allow diffusion of water vapour, whereas butyls and polysulfides have good water resistance, coupled with extremely low water vapour transmission rates.

Construction sealants are not designed to seal against chemicals, but can be exposed to them in use, for example, sealants subjected to road deicing chemicals or to chemicals used or stored nearby. Furthermore, many sealants are not exposed to aggressive chemicals in service, but are in manufacturing operations. Most electronics encapsulants experience only moderate temperatures and no chemical exposure in service, but commonly experience hot soldering operations and boiling solvent washes in production.

#### **3.4.5 UV Resistance**

UV resistance is very important in all types of joints exposed to the sun, including those used in construction and automotive glazing. Some sealants, such as silicones, are inherently UV resistant, whereas others, such as urethanes, must be shielded or have UV absorbers and inhibitors added to the formulations.

#### **3.4.6 Adhesion**

Although the main function of a sealant is to fill a void completely, adhesion to the joint surfaces is critical for most sealing applications (there are exceptions, for example, a gasket that is held under compression). Loss of adhesion in a threaded or overlap joint can allow a fluid to wick into the sealant-substrate interface, leading to increased degradation of the sealant, or corrosion of the substrate, or leakage. It can also allow vibration loosening of a threaded joint, ultimately leading to failure.

In a construction joint, any loss of adhesion causes the sealant to move away from the surface, leaving a gap. Even in a gasket sealed by compression, adhesion can be a benefit. Loss of tension in such a system, such as occurs in the relaxation of fasteners, will ultimately lead to failure. Strong adhesion to the flanges postpones the onset of that failure until debonding occurs.

A primerless sealant that will strongly and permanently adhere to every surface under every possible condition is not considered realistic, especially when the enormous range of surfaces is considered, along with all the possible surface contaminants. The sealant chemist endeavors to make a sealant as versatile as possible and builds appropriate self-bonding adhesion into the sealant system by incorporating such features as oil-cutting chemicals and adhesion promoters.

Adhesion promoters are molecules that diffuse to the sealant-surface interface and behave like oil-in-water emulsifiers. Part of their molecular structure is very compatible with the sealant, and another part is very compatible with the surface; thus, they act as a bridge between the two. In some cases, solutions of these adhesion promoters are used as surface primers prior to sealant application. Reactive silanes have been found to be versatile adhesion promoters for many sealant and adhesive chemistries. The term primer can encompass these adhesion promoters, cure

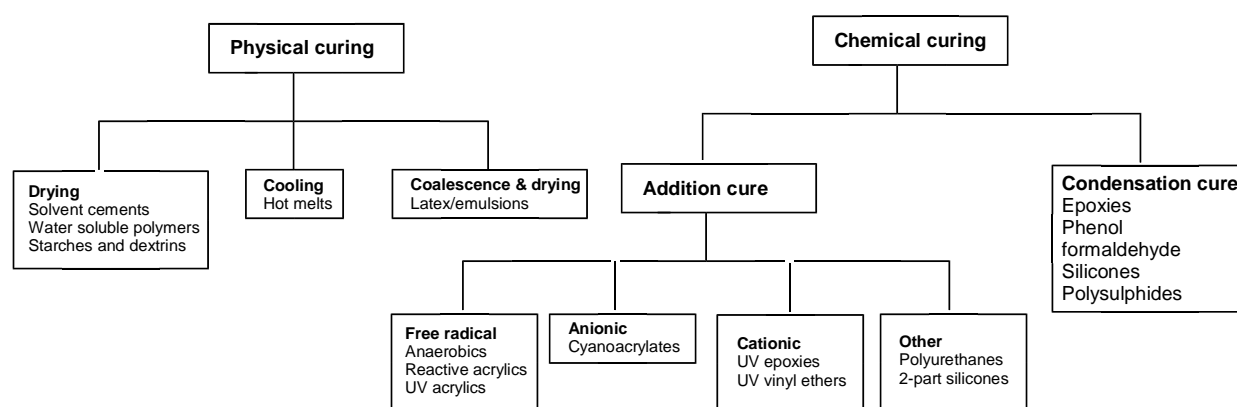
accelerators, corrosion-inhibiting primers and cleaners. The importance of bond preparation and cleanliness cannot be overemphasised, although more than simple abrasion or solvent wiping is not practical in many industries. In critical applications, such as aircraft assembly, such preparation is routine. Corrosion-inhibiting primers, such as phosphoric acid anodizing, are used prior to application of adhesion promoter and sealant in the aerospace industry.

### 3.4.7 Electrical Properties of Sealants

Most sealants are good insulators. In electronics and electrical applications that range from very low to very high voltage systems, special sealants with controlled dielectric constants, dielectric strengths and dissipation factors are available. A few sealants are deliberately made electrically conductive for sealing and gasketing assemblies where radio frequency (RF) and electromagnetic interference (EMI) shielding are important.

## 3.5 Curing of Adhesives and Sealants

Most adhesives and sealants are applied as liquids and then transformed or ‘cured’ into solids by chemical or physical means. Figure 3.1 shows examples of adhesives and sealant technologies that are cured by the two different routes.



**Figure 3.1 Curing mechanisms of adhesives and sealants**

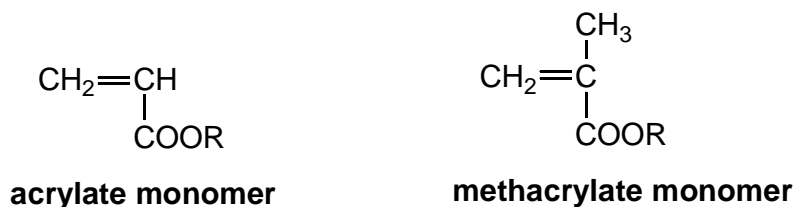
## References

1. G.S. Haviland, *Machinery Adhesives for Locking, Retaining and Sealing*, Marcel Dekker, New York, USA, 1986.
2. D.J. Dunn, *Engineered Material Handbook, Volume 3: Adhesives and Sealants*, ASM International, 1990, 48.

## 4 Adhesive and Sealant Materials

### 4.1 Acrylic Adhesives

Acrylic adhesives are characterised by the polymerisation of acrylate and methacrylate monomers.



One of the reasons that acrylic adhesives are so versatile is the vast range of monomers that are available commercially. Table 4.1 shows examples of these.

Table 4.1 Examples of monomers used in acrylic adhesives	
<i>N,N</i> -dimethylacrylamide	glycidyl methacrylate
2-ethoxyethyl acrylate	hexyl methacrylate
2-ethylhexyl acrylate	hydroxyethyl acrylate
2-hydroxyethyl acrylate	isopropyl methacrylate
2-methylcyclohexyl methacrylate	methacrylamide
2-phenoxyethyl acrylate	methacrylic acid
3-methyl-1-butyl acrylate	methyl acrylate
acrylic acid	<i>N</i> -methyl methacrylamide
benzyl methacrylate	methyl methacrylate
butyl acrylate	neopentyl glycol diacrylate
butyl methacrylate	neopentyl methacrylate
cyclohexyl acrylate	norbornenyl acrylate
cyclohexyl methacrylate	norbornyl diacrylate
dicyclopentenyl acrylate	phenyl acrylate
dodecyl acrylate	phenyl methacrylate
ethoxylated bisphenol A dimethacrylate	tetrahydrofurfuryl methacrylate
ethyl acrylate	triethylene glycol dimethacrylate
ethyl methacrylate	trimethoxysilyloxypropyl acrylate
ethylene glycol dimethacrylate	trimethylol propane trimethacrylate

In addition to simple monomers, isocyanates and urethane pre-polymers can be end-capped with hydroxyl acrylates and methacrylates to make oligomers called urethane acrylates and methacrylates. Epoxy resins can be reacted with unsaturated acids to give acrylate and methacrylate terminated oligomers.

Acrylic adhesives can be classified as single component or two-component. The former are exemplified by anaerobic adhesives, cyanoacrylates and ultraviolet light cured adhesives, whereas the latter are commonly called reactive acrylics. UV acrylics are covered in Section 4.5.

Anaerobic adhesives and cyanoacrylates appear superficially to be very similar in that they both cure spontaneously when confined between two surfaces. However, their chemistry and performance properties are very different as described below.

#### 4.1.1 Anaerobics

Anaerobic adhesives are single component acrylic adhesive systems based mainly on dimethacrylate and trimethacrylate monomers. The term ‘anaerobic’ was originally used to signify

that the adhesives would cure spontaneously when air was excluded and the adhesives are frequently referred to as simply ‘anaerobics’.

Anaerobic adhesives were originally developed by Loctite Corporation (now Henkel-Loctite) out of technology originally developed by General Electric. This technology was based on generating peroxy compounds in monomers by bubbling air or oxygen through them. Unfortunately, air had to be bubbled through them continuously to maintain stability. These products, known as Anaerobic Permafil, took a leap forward from two major events; firstly, the discovery by American Sealants Corporation that deliberately adding hydroperoxides and stabilisers could give stable systems, and secondly, the development of the low density polyethylene bottle, which had a very high oxygen permeability. These developments led to the successful introduction of bottles of single component anaerobic adhesives that could replace lockwashers and lock nuts and bolts tightly – American Sealants was subsequently re-named Loctite Corporation.

With hindsight, we now know that these systems are not truly ‘anaerobic’ systems but are free-radical redox systems where the hydroperoxide reacts with transition metals on the substrates, typically iron or copper, to generate free radicals, which then polymerise the monomers. However, as with most free radical systems, atmospheric oxygen is a strong retarder and thus the systems polymerise rapidly in an assembled joint, but will not cure if placed on a surface in the atmosphere.

A good way to look at anaerobics is to consider them as materials that behave in a completely opposite manner to a conventional air-drying oil paint. Oil paints are cured by contact with air whilst the curing of anaerobics is inhibited by air. The oil paint comes completely sealed in an air-impermeable tin-plated can and when brushed on a surface, it cures by reaction with atmospheric oxygen, accelerated by so-called metallic ‘driers’ in the paint. An anaerobic, on the other hand, is always supplied in a thin-walled low-density polyethylene bottle or tube, which is usually only half filled. This plastic is highly permeable to oxygen.

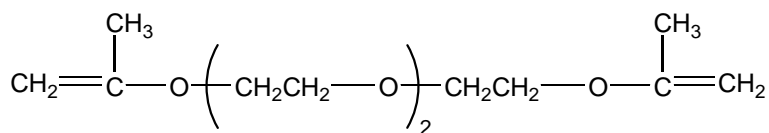
Anaerobics typically comprise:

- Monomers
- Initiators
- Accelerators
- Plasticisers
- Stabilisers
- Thickeners
- Fillers
- Other additives

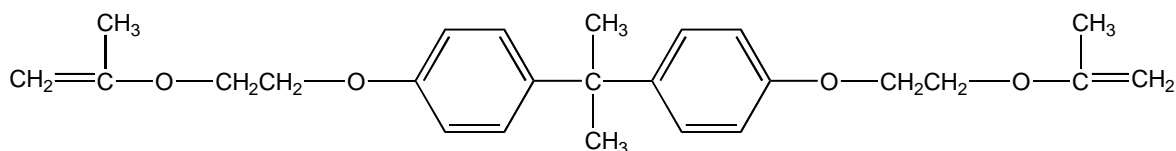
Although the range of useable additives is quite large, all additives have to be chosen and tested carefully. Anaerobics can be destabilised by certain types of impurities, for example, traces of transition metals such as iron or copper, peroxides and amines.

Anaerobics are usually formulated with di- or trifunctional methacrylate monomers that can be polymerised rapidly to form a tightly crosslinked thermoset polymer. Typical examples are triethylene glycol dimethacrylate, ethoxylated bisphenol A dimethacrylate and trimethylolpropane trimethacrylate. Other monomers are used to modify the properties. Examples are hydroxyethyl or hydroxypropyl methacrylate and acrylic or methacrylic acid, which help to adjust viscosity, cure speeds and adhesive strength.

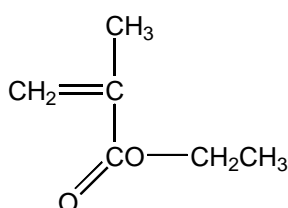




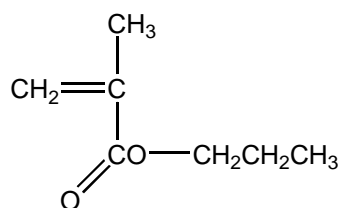
**triethylene glycol dimethacrylate**



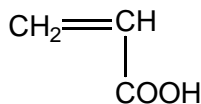
**ethoxylated bisphenol A dimethacrylate**



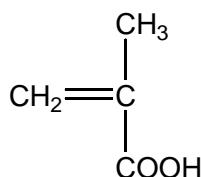
**hydroxyethyl methacrylate**



**hydroxypropyl methacrylate**



**acrylic acid**



**methacrylic acid**

Initiators (sometimes called catalysts) are typically hydroperoxides or peresters and function by generating free radicals by reaction with transition metals on the surfaces being bonded.

Accelerators are compounds that serve to speed up the curing process. Many such compounds have been developed over the years but the most widely used are aromatic amines, orthobenzoic sulfimide (saccharin) and acetyl phenyl hydrazine.

Plasticisers are used to lower the cost of formulations and to lower the compressive strengths. Sometimes high molecular weight monofunctional monomers serve as plasticisers, in most cases non-reactive glycol esters are used.

Stabilisers are used to enhance the role of oxygen in keeping the products shelf-stable. Common free-radical stabilisers are used including benzoquinone and hydroquinone. Also metal chelators have proved valuable in maximising shelf life – EDTA derivatives are the most common.

Thickeners are used to control the rheology of the adhesives and range from fumed silicas to soluble polymers such as acrylics and polyvinyl acetate.

Fillers are insoluble additives used to modify rheology and to enhance properties such as oil or solvent resistance.

Other additives are also frequently added such as dyes, pigments, heat stabilisers and lubricants.

Table 4.2 shows the advantages and disadvantages of anaerobics.

<b>Table 4.2 Advantages and disadvantages of anaerobic adhesives</b>	
<b>Advantages</b>	<b>Disadvantages</b>
Easy to use – one-component Fast curing at room temperature High bond strengths Excellent solvent and water resistance Temperature resistance to 180 °C Wide range of viscosities 100% solid – no solvents	Brittle Limited gap filling Cure rate very surface dependent Can stress crack some thermoplastics Very expensive

Their one-component nature and ability to cure at room temperature are huge benefits to any user and these are the unique features that distinguish them from all other high performance adhesives.

They are available in a wide range of viscosities from thin liquids to almost solid gels.

The use of multifunctional monomers in anaerobics leads to a highly crosslinked thermoset polymer that is heat resistant and has excellent oil and solvent resistance.

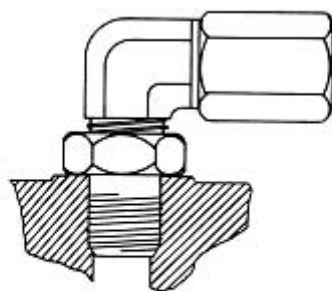
Anaerobics cure very quickly on clean iron, steel or brass surfaces where transition metal ions catalyse the initiation of polymerisation. However, they cure more slowly on plated surfaces, on oily surfaces or in the presence of certain rust-inhibiting chemicals, such as chromates. For very inactive surfaces or for fixturing on plastics, surface primer solutions (usually amines or copper salts) can be used.

The fact that the polymerisation of anaerobics is initiated from the surface of the substrates being bonded gives them a deficiency in common with cyanoacrylates (see Section 4.1.2 of this report), viz. a very limited gap filling capability. Primers have to be used to improve this situation, thus negating the one-component benefit of the adhesives.

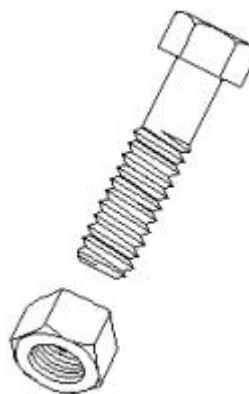
In common with many organic liquids, the liquid anaerobics can embrittle and stress crack some plastics and testing needs to be done before using them on plastics in general. Speeding up the curing with primers will often eliminate this problem.

Toughening of anaerobics by using urethane methacrylate monomers or by incorporating rubbers has been moderately successful, to create (expensive) structural adhesives. However, in contrast to other tough adhesives like reactive acrylics and polyurethanes, they remain relatively brittle materials.

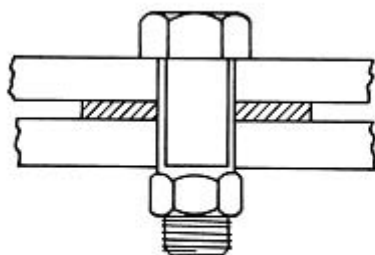
Figure 4.1 shows typical applications for anaerobics. Their first successful application was to replace lock washers in threaded fastener assemblies (e.g., nuts and bolts), where they fulfill the dual function of locking and sealing the assembly. Frequently referred to as liquid lock washers, anaerobics adhere strongly to the metal surfaces and prevent loosening from vibration. They also completely fill the void space in a threaded assembly and protect it against corrosion. This is still the most distinctive application for anaerobics because they do not merely act as a liquid alternative to lock washers but truly augment the assembly, particularly in situations under vibration, such as in vehicle applications. To remain effective, assembled fasteners must maintain strength under tension and the adhesion provided by an anaerobic increases the forces required to loosen the assembly. Furthermore, even if an assembly should loosen, the fastener will not disassemble completely (such as a screw falling out or a nut coming off), because the cured anaerobic completely fills the void spaces between threads – thus preventing catastrophic failures.



**Threaded pipe joint**



**Nut & bolt**



**Gasket**

**Figure 4.1 Applications for anaerobic adhesives**

Threadlockers can be formulated to have very low strengths, such as for small adjustment screws, medium strengths for assemblies requiring disassembly, or high strength for permanent assemblies.

In addition to liquid anaerobics, threadlockers are supplied in a solid form that can be pre-applied to a fastener. In these systems, the anaerobic adhesives or a catalyst are microencapsulated in a thin shell. A typical water-based slurry for applying such a system to fasteners consists of a water-soluble binder or emulsion, a dispersed anaerobic adhesive, and separate microcapsules of a peroxide and a transition metal salt. The slurry is applied to fasteners by the customer or a converter and is dry to touch after removal of the water. This pre-applied coating remains stable until a nut is applied to the fastener when the shearing action of engagement breaks the microcapsules and the adhesive cures, locking the fastener.

Although expensive, pre-applied threadlockers avoid the necessity of handling liquid anaerobics on a production line. Attempts have been made over the years to formulate microencapsulated systems that would be truly pre-applied adhesives for face-face bonding, but the need to thoroughly mix the monomers and catalysts has never been successfully overcome, except in the case of threaded fasteners.

Other important applications for anaerobics include the sealing of threaded pipe joints, gasketing, structural adhesives and the bonding of slip fitted cylindrical parts (often called 'retaining' compounds).

In pipe sealing, anaerobics are high performance alternatives to PTFE tape or pipe dopes and have approval for potable water systems worldwide. Indeed, Loctite's original 'Pipe Sealant with Teflon' has been copied by many companies and become an industry standard. Anaerobics lubricate a joint during assembly and have the ability to seal a wide range of thread styles and designs.

In gasketing, anaerobics compete with preformed rubber and composite gaskets and with RTV silicones. Being quite inflexible materials, anaerobics are best suited for flange designs that are not subjected to excessive movement. Anaerobics have proved popular in various powertrain applications by manufacturers of heavy trucks and off-road vehicles where their versatility allows a wide range of gasketing applications. The moulding of special pre-formed gaskets would not be cost effective for these relatively low volume applications.

Anaerobics for retaining applications are formulated for high adhesion and allow the use of slip-fits rather than push-fits. The most common application of retaining compounds is to assemble bearings onto shafts.

Anaerobics are also very effective porosity sealants for castings and powdered metals (see Section 5.8).

Loctite's basic patents on anaerobics began to expire in the 1970s. Up until that time they manufactured their own monomers and totally controlled the highly profitable business, with a strategy of manufacturing and selling in small quantities. With the expiration of patents, the wide availability of monomers on the open market and with the dissemination of 'anaerobic knowledge' around the world, many companies in many countries now manufacture anaerobics.

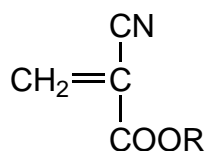
Henkel-Loctite is still the dominant supplier. Permabond and Three Bond also have significant sales in this area.

The global consumption of anaerobics is of the order of 4500 tons.

#### **4.1.2 Cyanoacrylates**

Cyanoacrylates were the world's first single-component 'instant' adhesives that bond almost everything, including the skin on users' fingers.

Cyanoacrylate adhesives are based on a special type of acrylic monomer. They are nominally esters of 2-cyanoacrylic acid:

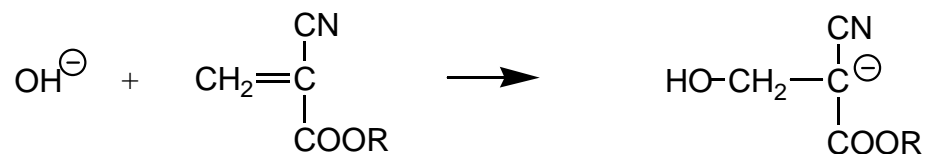
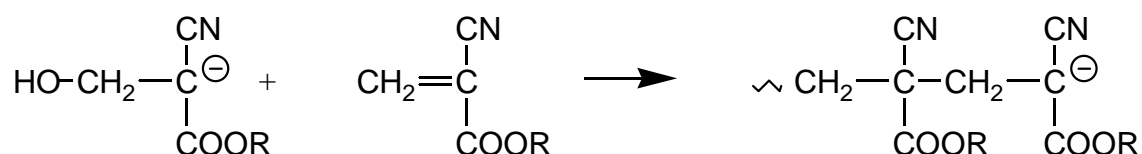


#### **2-cyanoacrylate**

where R is an alkyl group, e.g., methyl, ethyl, butyl, octyl, allyl, ethoxyethyl

Cyanoacrylates were invented by Dr. Harry Coover of Eastman Chemical in the early 1950s and Eastman 910 was introduced in 1958 as an industrial adhesive, but the real impetus for their market growth was when Crazy Glue and Superglue 3 were introduced as consumer products by Toa Gosei and Loctite in 1973-74. Eastman entered the consumer market in 1976 but eventually sold the business to Permabond in 1980.

The electron withdrawing (electrophilic) cyano group makes these monomers very susceptible to polymerisation by nucleophilic species, i.e., they polymerise anionically. Even very weak nucleophiles such as the OH<sup>-</sup> ions from atmospheric moisture on surfaces are sufficient to polymerise the monomers in seconds, when they are confined between two surfaces (Figure 4.2).

**Initiation****Propagation****Figure 4.2 Anionic polymerisation of cyanoacrylates**

The polymerisation does not normally have a termination step, in contrast to most other anionic polymerisations, which are very sensitive to trace impurities such as components of the atmosphere or moisture, only strong acids are terminating agents. Other initiators such as tertiary amines and phosphines have been postulated to polymerise via polymeric zwitterions. This mechanism has been proved by the isolation of stable zwitterions.

In practice, polymerisations of cyanoacrylates stop when monomer is exhausted, when the high viscosity of the polymerising systems prevents molecular diffusion, or when strong acids are present on the surfaces being bonded. Cyanoacrylates polymerise spontaneously to high molecular weights and coupled with their high polarity, this leads to very high adhesive and cohesive strengths.

Methyl cyanoacrylate was the first monomer to be used and was particularly useful for bonding metal substrates. It was largely superseded by ethyl cyanoacrylate in both industrial and consumer products, because of the versatility of the ethyl monomer in bonding a wide range of metals and plastics.

The thing that makes cyanoacrylates unique is the fact that when placed between closely fitting surfaces, they will cure to give a strong joint in as little as a few seconds. This feature made cyanoacrylates readily acceptable to consumers and was easily demonstrated in a 15 or 30 second TV commercial. The propensity of cyanoacrylates in bonding skin was never a hindrance to their market growth – the publicity regarding spectacular or embarrassing incidents only fuelled their acceptance as instant adhesives.

They also give very high tensile shear strengths on a wide range of metals and plastics (typically 15-30 MPa, 2000-4000 p.s.i.).

Cyanoacrylate adhesives are extremely sensitive to traces of impurities and must be manufactured, stored and used under controlled conditions. Basic impurities or contaminants can seriously affect the shelf life or stability of the adhesives, and conversely, acidic materials can slow down or completely inhibit curing. Peroxides or free-radical stabilisers in a potential additive can also seriously affect performance. Because of the sensitivity to contaminants, it is not possible to formulate cyanoacrylates with the wide range of thickeners, fillers and other additives that are available to formulators of other adhesive systems.

The simplest formulations for cyanoacrylate adhesives comprise:

- Monomer
- Thickener
- Acidic stabiliser
- Free radical stabiliser

The basic monomers are very thin (2-3 mPa.s) liquids, and adhesives formulated with these can be used to 'wick-in' to pre-assembled items such as for locking small adjustment screws. The adhesives can be thickened with specially purified acrylic polymers or fumed silica to produce high viscous or totally gelled materials.

Acidic stabilisers tend to be parts-per-million quantities of strong acids such as sulfuric or sulfonic acids. Cyanoacrylates can also cure free-radically like most other acrylic monomers, and free-radical stabilisers of the hydroquinone or benzoquinone type are used to maximise shelf life.

Table 4.3 shows the strengths and weaknesses of cyanoacrylates.

The curing of cyanoacrylates is catalytic and proceeds from the surfaces of the material being bonded. However, this does create a limitation to these adhesives in that as the polymerisation proceeds, diffusion of the propagating species is slowed down and effectively slows to zero if large bond gaps are involved. To improve gap-filling capabilities and get the ultimate in cure speed, cyanoacrylates can be accelerated with primers to give virtually instant fixturing and curing. Aromatic amines are very effective in this regard.

Because the cure is initiated from moisture on surfaces, curing can be very slow under very dry conditions, such as in winter and relative humidities above 40% are recommended for controlled bonding.

The polymerised cyanoacrylates are rigid thermoplastics with a glass transition temperature  $T_g$  of 100 °C. (Note that this is same as the thermoplastic, polystyrene.) As such they have very poor impact and peel strengths, particularly at low temperatures and have limited high temperature resistance.

Because of their thermoplastic polar nature, cyanoacrylates are not normally recommended for prolonged outdoor exposure (particularly on metals) or for exposure to aggressive polar solvents, although resistance to many solvents is quite good at ambient temperatures.

<b>Table 4.3 Advantages and disadvantages of cyanoacrylate adhesives</b>	
<b>Advantages</b>	<b>Disadvantages</b>
Easy to use – one-component	Difficult to manufacture
Very fast curing	Bond skin in seconds
High bond strengths	Irritating vapours
Bond a wide range of materials	High temperature performance to <100 °C
Wide range of viscosities	Brittle
100% solids – no solvents	Cure time affected by humidity
	Limited solvent and water resistance
	Limiting gap filling
	Expensive

Some of the traditional weaknesses of cyanoacrylates have been eliminated in recent years, although the major features of an adhesive tend to be dominated mainly by the backbone polymer of the adhesive.

#### *4.1.2.1 Low-Volatile Cyanoacrylates*

Cyanoacrylates have a very sharp odour and are strong eye and nasal irritants in enclosed spaces. The volatility of cyanoacrylate monomers like ethyl or methyl can also lead to the formation of a white haze, known as blooming, around the cyanoacrylate bond line. Blooming occurs when cyanoacrylate monomer volatilises and settles around the bond line in the form of white polymer deposits. In fact the blooming phenomenon is used in advanced fingerprint detection by police forces where objects that are difficult to extract fingerprints from are exposed to vapours of cyanoacrylate. Blooming can be mitigated by using lower volatile monomers, e.g., ethoxy ethyl or ethoxy methyl cyanoacrylate. These higher molecular weight monomers are less volatile than standard ethyl and methyl cyanoacrylates, do not have as strong an odour and are less likely to cause blooming.

#### *4.1.2.2 Surface-Insensitive Cyanoacrylates*

Although cyanoacrylates bond to most surfaces, making them very useful as general purpose industrial and consumer adhesives, they cure slowly on and do not bond well to acidic surfaces, two of which are wood or paper. To address this limitation, surface-insensitive cyanoacrylates were developed by adding agents such as silacrowns, crown ethers, and calixarenes to ethyl cyanoacrylates. A recent patent [1] shows that compositions containing both calixarenes and crown ethers give particularly fast fixture times on steel, epoxy, glass, and balsawood.

#### *4.1.2.3 Thermally Resistant Cyanoacrylates*

Cyanoacrylates cure to thermoplastic polymers and typically give very limited high-temperature performance. The Tg of polyethyl cyanoacrylate is around 100 °C, and bonds fail dramatically at temperatures close to this. Early attempts to improve heat resistance involved the development of cyanoacrylates with an allylic group in the side chain. These materials could be crosslinked through the allyl group, resulting in a thermoset polymer matrix. Unfortunately, such systems had to be clamped during the heat-cure step, as the cyanoacrylate would soften well below the temperatures required to initiate crosslinking. Subsequent developments in thermally resistant cyanoacrylate technology have involved the use of unique additives such as maleic or phthalic anhydrides to produce products that provide long-term bond strength at temperatures as high as 120 °C. Difunctional cyanoacrylates with improved heat resistance have been known for many years but their synthesis was multi-step and very expensive. Henkel have recently devised a much simpler procedure for producing the monomers [2].

#### *4.1.2.4 Toughened Cyanoacrylates*

Like other rigid thermoplastics, cyanoacrylates have poor impact strength and low adhesive peel strengths. A major breakthrough was the discovery that certain compatible rubbers, e.g., ethylene-acrylic rubbers could give adhesives with high impact strength. It was also unexpectedly found that these compositions had excellent hot strength, i.e., resistance to thermal degradation of strength properties, and also elimination of post-cure embrittlement or loss of toughness properties which occurs with cyanoacrylate adhesive bonds upon exposure to heat and then cooling to room temperature. These rubber-toughened cyanoacrylates are true one-component structural adhesives, although somewhat slower curing than regular adhesives.

#### *4.1.2.5 Bonding of Non-Polar Plastics*

Primers have been developed that enable cyanoacrylates to bond non-polar plastics and elastomers such as polyethylene, polypropylene and thermoplastic polyolefins (TPOs) (see Section 6.3.4 of this report for a description of this technology).

#### 4.1.2.6 Preventing Skin-Bonding

Japanese researchers have disclosed that additives such as long chain aliphatic alcohols, carboxylic acids and esters can give adhesives with less adhesion to skin, without compromising normal adhesive properties [3].

#### 4.1.2.7 Other

Cyanoacrylates are expensive adhesives that tend to be used for the assembly of small parts, where speed of assembly is a prime requirement.

They bond a wide range of rubbers, plastics and metals and are ideal, easy to use systems with good performance as long as their inherent limitations are recognised.

Henkel-Loctite has recently developed an interesting alternative type of system by making cyanoacrylate adhesives that also cure with UV radiation [4]. This type of system combines the ability of cyanoacrylates to cure virtually instantly in small gap situations and also to cure by UV in exposed areas. This system is expected to be used in many applications in rapid product assembly such as in the medical device industry.

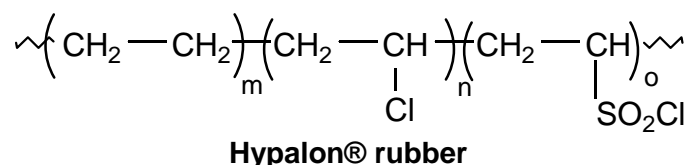
#### 4.1.3 Reactive Acrylics

Reactive acrylic adhesives are based on acrylic and methacrylic monomers, and polymerise free-radically similar to catalysed anaerobic adhesives. However, very significant differences exist. Whereas the monomers in anaerobics are predominantly difunctional or trifunctional in order to achieve highly crosslinked thermoset systems, reactive acrylics are based mainly on monofunctional monomers, e.g., methyl methacrylate or cyclohexyl methacrylate.

Reactive acrylics are differentiated from other two-component adhesive systems like epoxies or urethanes by the fact that the cure is catalytic, is relatively insensitive to the amount of catalyst used and does not depend on mixing precise stoichiometric amounts of adhesive and catalyst.

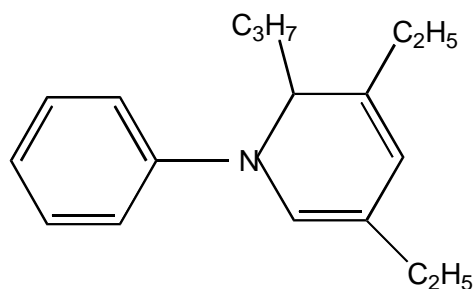
The earliest versions of these adhesives were based on methyl methacrylate cured by a benzoyl peroxide/aromatic amine redox cure system and were good for bonding thermoplastics such as polystyrene, ABS and unsaturated polyesters. They are very brittle materials but relatively inexpensive and are still used widely.

In the early 1970s, DuPont announced a family of patented adhesives based on solutions of their Hypalon® chlorosulphonated polyethylene rubber, that they called 'Reactive Fluids'.



They comprised essentially Hypalon® rubber dissolved in methyl methacrylate monomer and a peroxide or hydroperoxide initiator. They were cured using an activator second component, which was a crude mixture of an amine-aldehyde condensate, known as DuPont 808 – the active ingredient is a dihydropyridine, i.e., 3,5-diethyl-1,2-dihydro-1-phenyl-2-propylpyridine:





The activator and adhesive could be applied separately on the two surfaces to be bonded or laid on top of each other, prior to assembly. These adhesives were found to be outstanding at bonding unprepared or oily metals with fixture times varying from about one minute to several minutes. They were also tough adhesives with high impact and peel strengths because of the rubber component (see Table 4.4 for strengths and weaknesses).

Table 4.4 Advantages and disadvantages of reactive acrylic adhesives	
Advantages	Disadvantages
Very fast, controllable curing High peel strengths Bond unprepared surfaces Excellent plastics bonding Precise mixing not necessary 100% solids – no solvents	Two-component High temperature performance to 120 °C Odour and flammability Limited gap filling Limited fluid resistance

The adhesives have often been called tough acrylics or SGAs (second generation acrylics).

DuPont licensed their technology to several adhesive companies and collected royalties based on sales. This did in fact, lead to several innovations. Some were probably prompted by ‘getting around the patent’, others by the desirability of moving away from methyl methacrylate, which has a high odour and is very flammable, and others to avoid using the amine-aldehyde activator that had limited availability and produced dirty brown bondlines.

Low volatile versions were introduced, initially by Loctite Corporation, using higher molecular weight monomers such as tetrahydrofurfural methacrylate or cyclohexyl methacrylate and using a brush-on activator, based on a purified version of the amine-aldehyde condensate [5]. Other rubbers were also found to replace the Hypalon®, including ethylene-acrylic (AEM), styrene-butadiene block copolymers, polychloroprene and carboxylated nitrile. Although the low volatile versions did not develop the same strength as the methyl methacrylate bases ones, they were faster curing and very versatile in bonding a very wide range of materials.

These ‘consumer-friendly’ low volatile versions were introduced into the consumer market in the 1980s as Loctite Depend® and positioned as easy-to-use instant adhesives, without the skin bonding negative of cyanoacrylates or the slow curing and difficult to mix nature of epoxies.

When these adhesives were first introduced, some people went so far as to predict the total demise of the epoxy consumer adhesive. In fact, in both industrial and consumer markets, epoxies and reactive acrylics have both found their respective niches, corresponding to their strengths, with epoxies still being used mainly for metal bonding whilst acrylics have found wide use in high performance plastic bonding and for bonding oily metals.

The volatile, methyl methacrylate versions have continued to be used and, in fact, have become quite widely used in the automotive industry, particularly for bonding olefin-based substrates like automotive bumpers. ITW-Plexus is the major supplier to this market. High purity versions of the amine-aldehyde activator described above are now commercially available:

- Reilly PDHP from Reilly Industries, [www.reillyind.com](http://www.reillyind.com)
- Vanax® 808 HP from R.T. Vanderbilt, [www.rtvanderbilt.com](http://www.rtvanderbilt.com)

One other benefit of most types of reactive acrylics is the ability to be formulated to give adhesives that have a well defined induction time after contact of the adhesive and activator where no obvious thickening or curing takes place, followed by a very rapid fixturing and full cure of the adhesive. This feature is very beneficial where complex or large assemblies have to be bonded and a certain amount of time is necessary for assembly or positioning of parts.

Lord Corporation introduced adhesives containing methacrylated phosphate monomers that gave much-improved thermal and atmospheric durability. Dymax Corporation introduced so-called 'aerobic' acrylics that were less sensitive to inhibition by atmospheric oxygen. Table 4.5 shows the different types of reactive acrylics.

3M recently introduced two-part acrylic-based adhesives that can bond many low surface energy plastics, including many grades of polypropylene, polyethylene and thermoplastic polyolefins, without special surface preparation. These adhesives have one-component comprising an amine-complexed organoborane initiator, which is extended with a polyester adipamide and a second component comprising a toughened methacrylate monomer system. The major limitation of the 3M adhesives appears to be their cure time, with time to reach handling strength being 2 to 3 hours at room temperature and full cure in 8 to 24 hours – although heat can accelerate the reactions.

<b>Table 4.5 Major types of reactive acrylic adhesives</b>		
<b>Type of adhesive</b>	<b>Major ingredients</b>	<b>Distinctive features</b>
Methacrylate cements	Methyl methacrylate, benzoyl peroxide, aromatic amine	Very volatile, flammable, high odour, high strength, brittle
Reactive Fluids (DuPont)	Methyl methacrylate, Hypalon® rubber, dihydropyridine, hydroperoxide	Impact resistance, ability to bond oily metals and wide range of plastics. Very volatile, flammable, high odour
Low volatile systems (Loctite)	High molecular weight monomer, non-Hypalon® rubber, dihydropyridine, hydroperoxide	Low volatile, low flammability, fast fixture, able to bond wide range of materials
Methacrylated phosphates (Lord Corp.)	Methyl methacrylate, methacrylated phosphate, benzoyl peroxide, aromatic amine, carboxylated nitrile rubber	High adhesion to oily metals. Does not require dihydropyridine activators. Improved resistance to high temperature and humidity
Aerobic adhesives (Dymax Corp.)	Hydroxyfunctional monomers, dibasic acid, perester, dihydropyridine, urethane rubber, transition metal salt	Very fast curing, less sensitivity to inhibition by atmospheric oxygen
Graft copolymers (ITW-Plexus)	Methyl methacrylate, Hypalon, graft or core-shell polymers	Enhanced strength and toughness. Less stringing on dispensing
Structural Plastic Adhesive (3M)	Amine-complexed organoborane initiator, rubber toughened methacrylate monomer, polyfunctional aziridines	Low volatile. 10:1 mix ratio. Very slow fixture. Good adhesion to wide range of materials including polyolefins. Tough, environmentally resistant bonds.
Hypalon® is chlorosulphonated polyethylene rubber from DuPont Dow Elastomers		

In recent years, many reactive acrylic formulations have evolved to two-component formulations that are mixed in a 1:1 ratio. These developments have been encouraged by the development of syringe and cartridge dispensers fitted with static mixers. In some respect, these makes them similar to some of the epoxies that the 'no-mix' feature of acrylics was designed to supercede. These mixable systems are particularly effective in filling very thick bondlines. In these systems the distinction between adhesive and activator has been lost.

Some of these mixable systems use a variety of redox initiation systems but the original methyl methacrylate/Hypalon® systems are still cured by amine-aldehyde condensates.

Reactive acrylics are structural adhesives with a wide range of applications. They frequently compete with epoxies and polyurethanes. Applications include fibreglass and sheet steel bonding, magnets, loudspeakers, sporting goods, miscellaneous metal and plastics assembly, particularly when fast curing with no surface preparation is desired.

Limitations of these adhesives include high temperature resistance only to about 120 °C and limited resistance to very aggressive solvents. These aggressive environments are where high performance epoxies come into their own.

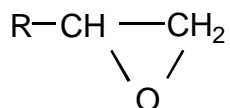
The major manufacturers of reactive acrylics are ITW Plexus, ITW Devcon, Lord Corp., Dymax and Henkel-Loctite, although as key patents are expiring, many other companies are entering the field.

No company has established very strong brand recognition in reactive acrylics. It is expected that many companies will start manufacturing these adhesives in the future and that the business will become similar to the epoxy adhesive industry with a lot of formulators.

## 4.2 Epoxies

Epoxies are thermoset resins normally prepared by reacting two-components. The first component consists of an epoxy resin and the second is the epoxy curing agent, often called a hardener.

Epoxy resins are difunctional or multifunctional resins containing more than one epoxide group. The epoxide group is also called an oxirane ring or glycidyl group:



Epoxy resins were invented by a Swiss chemist, Dr. Pierre Castan and patented in 1939. The Swiss company Ciba Geigy carried out the commercial development of epoxy adhesives in the 1940s.

There are two main categories of epoxy resins, namely the glycidyl epoxy, and non-glycidyl epoxy resins. The glycidyl epoxies are further classified as glycidyl-ether, glycidyl-ester and glycidyl-amine.

Glycidyl epoxies are prepared via a condensation reaction of a dihydroxy compound, dibasic acid or a diamine and epichlorohydrin.

Non-glycidyl epoxies are either aliphatic or cycloaliphatic epoxy resins. They are made by peroxidation of an olefinic double bond. Cycloaliphatic epoxies have recently become important for the preparation of UV cured adhesives and coatings (see Section 4.5).

Epoxy adhesives can be one-component adhesives that are heat cured, but are most commonly used as two-component systems comprising a resin portion and a hardener portion. The curing reaction

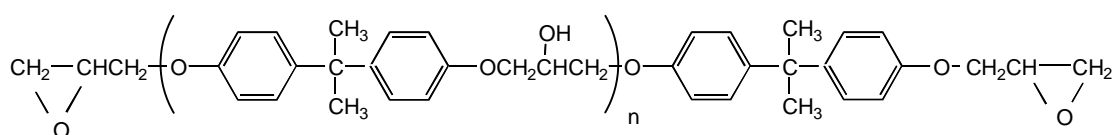
can be a condensation reaction involving reaction of the oxirane groups and hydroxyl groups with the hardener, or it can be a catalytic reaction involving cationic polymerisation of the oxirane groups.

A typical two-component epoxy adhesive comprises:

- Epoxy resin
- Hardener
- Fillers
- Plasticisers
- Accelerators
- Reactive diluent
- Toughening agents

The epoxy resin and hardener are kept separated in the two-components of the adhesive, but the other components can be formulated into either portion to adjust the viscosity and help in adjusting the mix ratio of the two-components.

The most commonly used epoxies in adhesives are based on the diglycidyl ether of bisphenol-A (DGEBA) (the term bisphenol A denotes the bisphenol of acetone).



**DGEBA, where n = 0-3 for liquid resins and 3-30 for solid resins**

The most common resins used in the adhesives industry are based on DGEBA where n = 0.14 for liquid resins, known under the trade names of Dow 331, Ciba (now Vantico) 6010 and Shell (now Resolution Performance Products) 828.

Plasticisers can be used but reactive diluents based on monofunctional epoxies are the most common additives to reduce brittleness.

There are several different types of hardeners used in the condensation curing:

- Aliphatic amines
- Amidoamines
- Aromatic amines
- Cycloaliphatic amines
- Imidazoles
- Polyamides
- Anhydrides
- Polysulfides
- Dicyandiamide (DiCy)
- Boron trifluoride adducts

The cure kinetics and the Tg of the cured resin are dependent on the molecular structure of the hardener.

Amines and polyamides tend to give the fastest cures but there are concerns over the toxicity of many amines. Polysulfides of the Thiokol® or Capcure® type give quite flexible systems, cure the resins rapidly at room temperature and are used quite widely in consumer adhesives. New versions of these have recently been prepared by Cognis Corporation ([www.cognis.com](http://www.cognis.com)), that have

considerably reduced odour. Anhydride hardeners give outstanding electrical properties at high temperatures but tend to be very slow curing systems.

In all cases, precise measuring of resin and hardener is essential to enable the condensation reactions to go to completion – this is one of the negatives of epoxy adhesives. Many application systems are now available that allow pre-measured amounts of resin and hardener to be dispensed and mixed. These include syringes, cartridges and automated meter-mix systems. Heat is often required to maximise the properties of two-component epoxies.

Catalytic curing of two-component epoxies can be achieved using cationic initiators such as  $\text{BF}_3$  adducts. Almost instantaneous cationic polymerisation of epoxies can be achieved with catalyst systems involving the reaction between organic halides and silver salts [6].

One-component epoxy adhesives can be formulated using dicyandiamide (DiCy) as the hardener. DiCy is called a latent hardener because it is insoluble in epoxies at ambient temperatures and only becomes soluble and active when the systems are heated. These types of epoxies have become widely used in the automotive industry for hem-flange bonding.

The versatility of epoxy resin systems arises from the large number of combinations of epoxy resins and hardeners, each of which gives a different cure profile and results in a different molecular structure in the resulting polymer. Compared to some other adhesive systems, such as cyanoacrylates or anaerobics, epoxies are not very sensitive to impurities. This gives tremendous scope for modification of their properties by additives, modifiers, fillers, rubber tougheners, plasticisers and other polymers to customise the adhesives for specific applications.

Many fillers can be used in epoxies, including:

- Calcium carbonate
- Marble flour
- Mica
- Silica
- Slate flour
- Vermiculite
- Zircon
- Aluminium
- Alumina
- Precious metals
- Glass microspheres
- Phenolic microspheres

Fillers usually confer beneficial properties such as reducing the cost of formulations, reducing shrinkage on curing, reducing moisture absorption, increasing compressive strength and modulus, increasing thermal or electrical conductivity, and increasing heat resistance. However, the negatives of fillers include increased weight, decreased impact and tensile strengths and loss of transparency.

Epoxies are quite versatile, high strength adhesives with excellent performance on metals, ceramics and glass. They will fill very large gaps, which is a major advantage over alternative systems like reactive acrylics and cyanoacrylates and have excellent thermal and fluid resistant properties. Table 4.6 shows their advantages and disadvantages.

**Table 4.6 Advantages and disadvantages of epoxy adhesives**

Advantages	Disadvantages
High bond strengths Excellent gap filling Bond a wide range of materials Excellent solvent and water resistance Excellent heat resistance Readily filled 100% solids – no solvents	Two-component – require precise mixing Slow curing Somewhat brittle Limited performance on plastics Strength reduced on dirty surfaces Very low viscosities unattainable Some hardeners are toxic Many hardeners have high odour

Disadvantages include their two-component (or heat cure) form, their inherent lack of toughness and limited performance on plastics, where reactive acrylics, cyanoacrylates and polyurethanes are usually superior. Also, because the base resins are relatively high molecular weight species, it is not possible to formulate very low viscosity adhesives, unless reactive diluents are added, with a corresponding drop in performance.

Epoxy adhesives can be toughened using reactive elastomers but do not attain the flexibility and toughness achievable with alternative adhesive technologies, such as reactive acrylics or urethanes. The primary elastomers used have been functionalised butadiene-acrylonitrile copolymers. These elastomers are available with epoxy-terminated (ETBN), carboxy-terminated (CTBN), amino-terminated (ATBN) and vinyl-terminated (VTBN) functionalities.

The relatively high viscosity of epoxies limits some applications but does enable film versions of adhesives to be easily made. Film adhesives are heat cured.

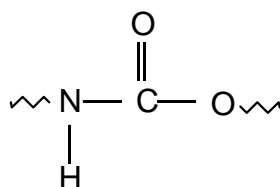
Epoxy resins are highly crosslinked thermoset systems that are used in a wide range of industries for structural adhesives, potting materials and encapsulants. Use in adhesives is in fact a relatively minor use for epoxies – the volumes used in coatings and flooring compounds are much larger.

There are many manufacturers of epoxies. Major ones include Vantico (formerly Ciba Geigy), Dow Automotive, 3M, Sumitomo Bakelite and Bakelite AG.

### 4.3 Urethanes

Although the birth of polyurethane chemistry can be traced back to the first synthesis of aliphatic isocyanates in the mid 19<sup>th</sup> century by Wurtz, the work of Otto Bayer in Germany in the 1930s led to the development of modern polyurethanes. Polyurethanes can be formulated as both adhesives and sealants

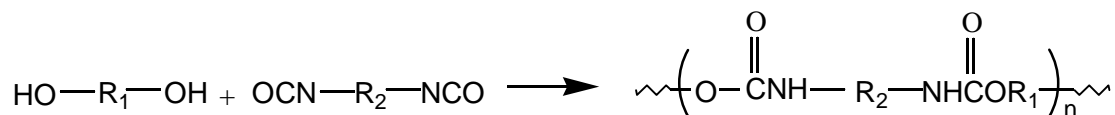
Polyurethane adhesives are based on polymers that contain urethane linkages in the molecular backbone, regardless of the chemical composition of the rest of the chain:



Thus a urethane adhesive can be based on a wide range of polymers as long as they can be reacted to form a urethane linkage. In practice, polymers can contain aliphatic and aromatic hydrocarbons, esters, ethers, amides, urea and allophanate groups. This leads to a very wide range of raw

materials being available and formulations tend to differ in the type of polymer used rather than on the variations in additives as seen with many other adhesives.

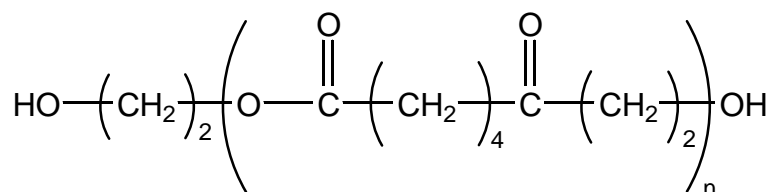
Polyurethanes are generally prepared by the reaction of a polyol with an isocyanate. The isocyanate group reacts with the hydroxyl groups of a polyol to form the repeating urethane linkage:



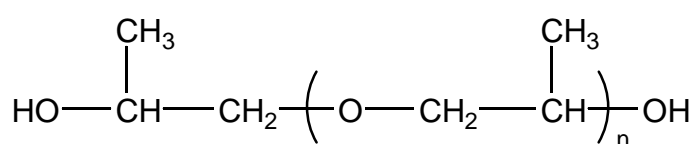
This is an addition reaction and, in contrast to polycondensation, there are no by-products of this reaction, although stoichiometry is important to control the nature and concentration of desired end groups. Polyurethanes may be prepared with hydroxyl or isocyanate end groups.

In general there are two types of commercial polyurethane adhesives, rigid and flexible. The rigid products are based on polyester polyols that give urethanes with very good adhesion, and have high strength, modulus and hardness. Flexible urethanes are based on polyether polyols that have low modulus and good low temperature properties. Polyether polyols are usually lower cost materials and used widely in sealants.

Commercial polyether polyols are generally limited in monomer composition to propylene oxide, ethylene oxide, butylene oxide and tetrahydrofuran. Industrial polyester polyols, many of which are the condensation products of organic acids and alcohols, may be prepared by a great many more combinations of monomers and thus add to the potential versatility of polyurethane products. The most common are based on adipamides.

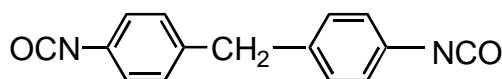


**polyester polyol**

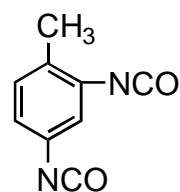


**polyether polyol**

The most commonly used isocyanates in polyurethane adhesives are aromatic, such as MDI (methylene diphenyl diisocyanate) and TDI (toluene diisocyanate).



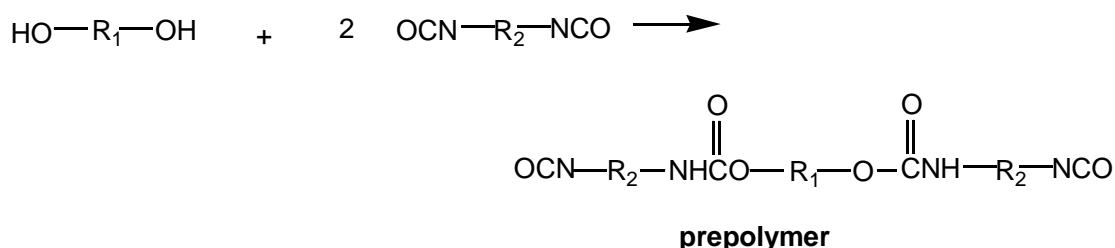
**MDI**



**TDI**

Aliphatic isocyanates are also used but in smaller volumes because of higher cost. Typical examples are hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPD) or hydrogenated MDI.

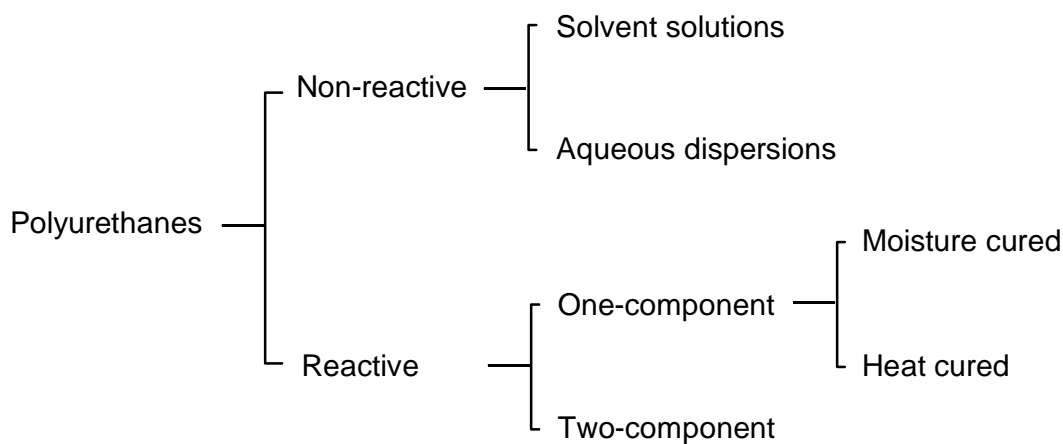
For the preparation of many polyurethanes, a two-step synthesis is preferable where a pre-polymer is formed with isocyanate end groups and then chain-extended to a higher molecular weight polymer by further reaction with short chain diols or diamines. For example, reaction of 1 mole of polyol with 2 moles of isocyanate will give an isocyanate-terminated prepolymer:



Note that isocyanates can also react with water to form a urea linkage and liberate carbon dioxide as a by-product. Thus, it is very important in adhesives to keep the components very dry to ensure maximum reaction of hydroxy and isocyanate groups and minimise void formation caused by CO<sub>2</sub> evolution.

Linear thermoplastic polyurethanes may be obtained by using compounds with two reactive groups such as diisocyanate and diols. Crosslinkable systems can be formed in one of two ways – either by using an excess of isocyanate in the reactions where the excess isocyanate can react with urethane groups in the polymer to form allophanate crosslinks, or by using multifunctional polyols or isocyanates. Crosslinking is particularly important for structural adhesives to stop them creeping under load.

Polyurethane adhesives can be non-reactive types or reactive types:



#### 4.3.1 Non-Reactive Adhesives

Polyurethane solvent borne adhesives consist of a high molecular weight hydroxy terminated polyurethane dissolved in a solvent. They are prepared by reacting a high molecular weight polyester diol with a diisocyanate. The polymer solutions are applied to both surfaces to be bonded and the solvents are allowed to evaporate. The surfaces are then pressed together, often using a heated nip roll.



Polyurethane aqueous dispersion adhesives are high molecular weight polyurethanes dispersed in water. They are applied and used in exactly the same manner as solvent-borne systems with the benefit of not using hazardous or flammable solvents.

### **4.3.2 Reactive Adhesives**

#### **4.3.2.1 One-Component Adhesives**

There are two types of adhesives in this category - moisture cured products and heat cured products.

Moisture cured products use a liquid isocyanate-terminated polyurethane with a relatively high molecular weight and a prepolymer with a low residual isocyanate content. The prepolymers are prepared by reacting an excess of isocyanate with high molecular weight polyester or polyether polyols. The free isocyanate groups react with moisture from the environment to form urea linkages. If the functionality of the prepolymer is larger than two (i.e., contains more than two isocyanate groups per molecule) the cured film will be chemically crosslinked. Adhesives of this type can be allowed to cure by atmospheric moisture or in some case are misted with water to speed up the curing. Unmodified aromatic isocyanates (predominantly MDI) are used as one-component binders to manufacture oriented strand board (OSB), medium density fibreboard (MDF) and particleboard. For these boards, the isocyanate is blended with wood strands, fibres and chips, respectively. The cure takes place in a press at about 200 °C. The curing reaction is predominately via the reaction with water with the formation of urea groups.

Heat cured adhesives use blocked isocyanates, where the isocyanate groups are reacted with agents such as  $\epsilon$ -caprolactam, methylethylketoxime, 3,5-dimethyl pyrazole and diethyl malonate. The blocking agents are released by heat thus liberating the isocyanate groups that can then react with hydroxy groups from a polyol. The high temperatures for unblocking (80 to 160 °C) have led to the major use of this technology in metal coatings and adhesive applications are limited.

#### **4.3.2.2 Two-Component Adhesives**

These adhesives consist of two relatively low molecular weight components: the polyol and the isocyanate. The components are mixed together to cure to a polyurethane. These types of adhesives are much faster curing than one-component systems.

Aromatic isocyanates (predominantly MDI) are used as one-component binders to manufacture oriented strand board (OSB), medium density fibreboard (MDF) and particleboard. For these boards, the isocyanate is blended with wood strands, fibres and chips, respectively. The cure takes place in a press at about 200 °C. The curing reaction is predominately via the reaction with water with the formation of urea groups.

Polyurethane adhesives are inherently quite flexible without added tougheners. Even the crosslinked polymers behave somewhat like thermoplastic elastomers with two-distinct phases – the hard phase contributed by the isocyanate and the soft phase from the polyol.

Polyurethanes do not have the extreme high performance of highly crosslinked epoxies or anaerobics or the instant curing of the cyanoacrylates. However, they are extremely versatile systems that can be formulated from hard to very flexible systems to form tough bonds with high peel strength (see Table 4.7). In many large-area bonding situations they compete with reactive acrylics. They have also replaced polychloroprene contact cements in many applications.

**Table 4.7 Advantages and disadvantages of polyurethane adhesives**

<b>Advantages</b>	<b>Disadvantages</b>
High bond strengths Excellent gap filling Bond a wide range of materials Good moisture resistance Inherently very flexible/tough 100% solids systems available	Slow curing of one-component systems Two-component systems require precise mixing Strength reduced on dirty surfaces Toxicity and irritancy of isocyanates Sensitive to residual moisture Range of additives restricted Relatively expensive

Based on their outstanding properties, their simple and economical processing and their high strength and flexibility, polyurethane adhesives have found broad use in many application areas. The segments in which polyurethane adhesives are used most are: the footwear industry, construction, woodworking, transportation, packaging and assembly operations.

Typical applications include:

- Shoe manufacture – replacing solvent based polychloroprene
- Bonding panels
- Packaging lamination
- Bonding fibreglass
- Automotive windshield bonding
- Construction adhesives

PU adhesive suppliers include Dow Automotive, Ashland, 3M, Rohm and Haas, and Bostick Findley.

#### **4.3.2.3 Urethane Sealants**

Urethane sealants are moisture cured one-component urethanes. Urethane sealants are one of the leading and fastest growing sealants in the non-glazing segment of the construction market and possess most of the desirable properties displayed by silicones (good flexibility, low compression set, good weatherability, and very low shrinkage). Excellent primerless adhesion is obtained on most surfaces. Although joint movement capability (typically  $\pm 25\%$ ) is not as good as with silicones, it exceeds that of all other sealant types. Tremco (US) and Sika (Switzerland) are the leading global suppliers of polyurethane sealants.

Unfortunately, polyurethanes tend to be more expensive than competing chemistries, and the rising price of oil is also forcing the cost of the raw materials upward. Continued high growth of polyurethanes is expected, but competition from alternative chemistries, such as high performance latices, is expected to restrain their growth somewhat.

Tremco (US) and Sika (Switzerland) are the leading global suppliers of polyurethane sealants.

## **4.4 Hot Melts**

Hot melt adhesives are 100% solid one-component systems that are applied in a molten state and solidify by cooling. Since they do not contain a carrier material such as a solvent or water, they are inherently fast-setting materials, often faster than instant adhesives like cyanoacrylates.

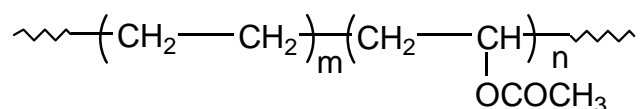
Hot melts can be dispensed in stick form from handguns or in bulk from semi-automatic or automatic application systems.

The overall formulation of most hot melt adhesives comprises:

- Base polymer – major ingredient, determines overall properties
- Tackifying resins – improve tack and adhesion
- Waxes and oils – lower viscosity, affect surface melting
- Plasticisers – lower viscosity, soften polymers
- Fillers – affect viscosity and bond strength, lower costs.
- Antioxidants – maintain hot stability of adhesive.

The base polymers determine most of the overall properties of the adhesive. These base polymers can include ethylene-vinyl acetate copolymers (EVA), low-density polyethylene (LDPE) and styrenic block copolymers (SBCs).

The most common base polymer is EVA:



Amorphous polyolefins (APOs) are also very important base polymers. Atactic polypropylene is a particularly useful polymer that is a by-product of the polymerisation of crystalline polypropylene.

Styrenic block copolymers are particularly useful for making pressure-sensitive hot melts.

Hot melt adhesives are thermoplastic adhesives that have some unique benefits, but some real weaknesses (Table 4.8).

Table 4.8 Advantages and disadvantages of hot melt adhesives	
Advantages	Disadvantages
Easy to use – one-component	Moderate bond strengths
Fast fixture	Many brittle at low temperatures
Good gap filling	Surface sensitive adhesion
Always ‘cure’	Strength sensitive to open time
100% solid – no solvents	Heat may damage sensitive substrates
Can be made rigid or flexible	Poor environmental resistance
	Heat resistance to 85 °C

Important characteristic of hot melts are their open time and their green strength. Open time is the time after application that the adhesive remains fluid enough to wet the second surface and create an effective bond. Green strength is a measure of the rate of solidification of the adhesive and is normally determined as the time to reach handling strength of the parts. In general there is a symbiotic relationship between a short open time and a high green strength. Also, the longer an adhesive is left open, the thicker it gets and its ability to wet a surface goes down, leading to a drop in bond strength.

Hot melts are not structural adhesives for bonding highly stressed or load bearing applications but are easy to use, medium strength, versatile adhesives that typically give tensile shear strengths of 1 to 7 MPa (150 to 1000 psi) on most surfaces. They are not as generally surface insensitive as some other adhesives and tend to be formulated to bond particular types of surfaces, e.g., plastics, metals, paper, etc.

Being thermoplastic systems, and based mainly on EVA polymers, their heat resistance and environmental resistance are moderate at best.

One concern that users often have with hot melts is the high temperatures (160-180 °C) required for melting and application. The heat can damage heat sensitive materials and is also a potential safety hazard. In recent years lower melting products (110-120 °C) have become available, particularly for packaging operations.

Recent innovations include the development of hydrophilic hot melts [7]. These are manufactured from several types of polymers and incorporate high levels of surfactants to enhance hydrophilicity. They are particularly useful for bonding to substrates that are typically employed in the construction of disposable nonwoven articles such as diapers (nappies). They maintain acceptable wet bond strength following exposure for prolonged periods of time to water, urine or similar materials. At the same time, such adhesives, being hydrophilic, do not hinder fluid transfer into the absorbent core of such articles.

Hot melts are used in a wide range of industries. The major application areas are:

- Packaging
- Labelling
- Woodworking
- Bookbinding

In the packaging industry, hot melts are used for applications such as sealing cases and cartons, tray forming, making deep-freeze boards and bonding sift-proof packs.

Labelling adhesives are not pressure sensitive systems but are regular thermoplastic hot melts applied using high speed wrap-around labelling machines. Labels are fed from magazine or roll feeders with the adhesive being applied to the leading and trailing edges of the label. In the food and beverage industry, hot melts can be designed to bond to cans, jars and bottles with the capability to handle hot, cold or wet surfaces.

Woodworking adhesives are used for a number of applications. Including edgebanding, soft forming, profile wrapping and V-grooving. The ability to bond to a wide range of substrates is important in this industry where materials include melamine-impregnated paper, high pressure laminates, wood veneer, polyester, ABS, polyester and PVC. Adhesives are often highly filled with inorganic fillers in this market, which serves to lower costs and adjust the rheology of the products.

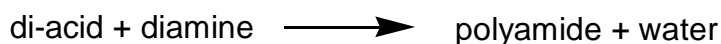
Bookbinding adhesives include versions for applications to the spines in perfect binding machines and pressure sensitive adhesives suitable for the so-called tipping in of removable inserts into newspapers or magazines.

In addition to regular formulated hot melts, several speciality versions are available. These include:

- Polyesters and copolyesters
- Polyamides and copolyamides
- Polyester-amide copolymers
- Hot melt polyurethanes
- Reactive hot melt polyurethanes (RHMU)

#### **4.4.1 Copolyamides**

Copolyamides can be made using the condensation of di-acid and diamines similar to the synthesis of nylon 6/6, or can be copolymers of rigid nylon 6 and the more flexible nylon 12 produced by the simultaneous ring-opening polymerisation of caprolactam and laurolactam.



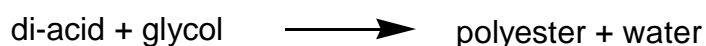
The properties and melting points can be altered by adjusting the copolymer composition and the molecular weight.

The di-acid-based adhesives are noted for their good balance of tensile strength and elongation, outstanding adhesion to a wide variety of substrates, including metal, wood, plasticised PVC and corona treated olefin films. They also have exceptional oil and grease resistance, low viscosity and fast set up time. Uses include the manufacturing of filters, footwear, cabinets, furniture and many other products. The nylon-type copolymer adhesives exhibit excellent resistance to dry cleaning solvents, good cold water wash resistance and excellent adhesion to various textiles.

Producers of copolyamides include Arizona Chemical, Bostik Findley and Atochem.

#### **4.4.2 Polyesters and Copolyesters**

Polyesters and copolyesters are similar in that they both have a carboxylate ester in the repeating unit and they are both alternating copolymers of a glycol and a di-acid. However, copolyesters contain more than one type of di-acid and/or glycol.



Developed originally in the 1950s by Bostik (now Bostik Findley) for the manufacturing of footwear, products are available with melting points from 65 °C up to 220 °C and ranging from completely amorphous to highly crystalline. Atochem is also a major producer of these types of adhesives.

#### **4.4.3 Polyurethanes**

These consist of high molecular weight hydroxyl-terminated polyurethanes, similar to the polymers used in solvent-based polyurethanes. They are most commonly applied as adhesive film in lamination types of applications.

#### **4.4.4 Reactive Hot Melt Urethanes (RHMUs)**

These are two stage thermoset adhesives that are applied as molten liquids and subsequently crosslink after application through reaction with atmospheric moisture. They have found many industrial applications due to their ability to bond to many substrates, good high temperature resistance compared to conventional thermoplastic hot melts, very good cold flexibility, excellent water and vapour resistance, and better solvent resistance.

RHMUs are based on the end capping of high molecular weight polyester or polyether polyols with isocyanates. Typical examples are polyhexamethylene adipate glycol and polytetramethylene ether glycol, end-capped with methylene diphenyl diisocyanate (MDI), and having a low number of free isocyanate groups. The polyester polyols tend to give harder more durable adhesive resins, whereas the polyether polyols are more flexible but less durable. In contrast to regular EVA or polyolefin based hot melts where a formulator buys and mixes a range of materials, manufacturers of RHMUs

buy polyols and isocyanates and prepare their own polymers. After preparation the polymers must be stored and packaged under dry conditions. RHMUs must be dispensed in special applicators with blanketing of the systems with dry nitrogen, and the cost of these systems can be prohibitive to small users. Just as with thermoplastic hot melts, open time and green strength are important characteristics of RHMUs. Green strength is perhaps more important here compared to regular hot melts in that this is the ultimate strength of the assembly until the moisture-induced crosslinking reaction takes place (can take up to 72 hours for completion, depending on atmospheric humidity and temperature).

Major applications for RHMUs include the assembly of large panels for recreation vehicles and caravans and the bonding of steel panels with an expanded polystyrene core for the production of insulated garage doors.

The global market for hot melts is over 950,000 tons.

The Western European market for hot melts, estimated at 267,000 tons in 2000, will grow 3.7%/year, to 308,000 tons by 2004, according to a recent study by IAL Consultants (London) ([www.ialconsultants.com](http://www.ialconsultants.com)).

Paper and packaging account for two-thirds of European hot melts consumption, followed by woodworking, tapes, and labels, according to IAL.

Important large manufacturers of hot melts include Henkel, H.B. Fuller, National Starch, Rohm and Haas, Beardow and Adams (UK), and Jowat.

## **4.5 Radiation Curing Systems**

Adhesive systems which use UV or visible light to begin curing are intrinsically very attractive systems to the manufacturing engineer, allowing assembly of components and then ‘curing on command’ by exposing to the UV irradiation. UV adhesives have been marketed for about 30 years with many successful applications in several market segments. High energy electron beams have also been used to cure adhesives, but market penetration has been limited.

### **4.5.1 Basic Chemistry of UV Systems**

All UV cured systems are based on an addition cure polymerisation whereby a free radical or cation adds to a carbon-carbon double bond or an oxirane ring and a chain reaction leads to formation of a polymer. The combination of monofunctional and multifunctional monomers or oligomers gives rise to crosslinking reactions, which contribute strength, heat resistance, and fluid resistance to the formulations.

Although commercial formulations contain many components, the essential elements of a UV system are the monomer (or functional oligomer), the photoinitiator and the source of UV energy (see Table 4.9).

<b>Table 4.9 Components of UV curing systems</b>		
	<b>Cationic systems</b>	<b>Free-radical systems</b>
<b>Monomers</b>	Cycloaliphatic epoxies Vinyl ethers Vinyl ether esters	Acrylates Methacrylates N-Vinyl pyrrolidone
<b>Oligomers</b>	Urethane vinyl ethers	Epoxy acrylates Epoxy methacrylates Urethane acrylates Urethane methacrylates Polyester methacrylates Polyether methacrylates
<b>Photoinitiators</b>	Aryl sulfonium salts Aryl phosphonium salts	Benzoin ethers Benzil ketals Acetophenones Benzophenone Phosphine oxides

#### 4.5.1.1 Free-Radical Systems

##### *Monomers and Oligomers*

There are two types of acrylic monomers used in UV systems, acrylates and methacrylates.

A wide range of monofunctional (one reactive group per molecule) and multifunctional (more than one reactive group per molecule) monomers are available, giving wide flexibility in formulating these systems. The simplest members of these families are acrylic and methacrylic acid, which have been used as adhesion promoters, particularly for metal substrates. Acrylates are the most widely available and they are used extensively for coatings. They are characterised by high cure speed, hard brittle coatings and often have severe skin irritation properties. Methacrylates have been used more extensively by adhesives formulators because of better adhesion properties, more flexible formulations and low skin irritancy. In general, methacrylates cure more slowly than acrylates. Free radically cured systems are very versatile but can be inhibited by atmospheric oxygen and some reducing agents.

In general, the use of monomers alone in these systems leads to fast-curing, highly crosslinked, brittle polymers. The incorporation of oligomers, where the reactive groups are grafted or terminated on to short chain length polymers, allows the incorporation of the properties of other polymers into the formulation. For example, the use of urethane acrylates or urethane methacrylates can yield very flexible or very tough formulations depending on the nature of the urethane. Both aromatic and aliphatic urethanes are readily available in a wide range of molecular weights and functionalities. Other oligomers include polyester, polyether, and polybutadiene acrylates and methacrylates.

##### *Photoinitiators*

These compounds are chosen to be stable in the formulations but rapidly decompose on irradiation by UV light. Photoinitiators generate free radicals in two ways under irradiation: a Norrish type 1 mechanism which is a homolytic cleavage of a carbon-carbon single bond leading to two free-radicals, or a Norrish type 2 mechanism which involves hydrogen abstraction from the initiator to generate radicals. This abstraction can be within the same molecule ('unimolecular intramolecular') or between two molecules ('bimolecular intermolecular').

Many compounds have been studied over the last 30 years but the most common photoinitiators in UV adhesives and coatings are:

- a. 1-hydroxycyclohexyl phenyl ketone. Sold commercially by Ciba Specialty Chemicals, as Irgacure 184. This is a substituted acetophenone and decomposes by a Norrish type 1 mechanism to produce free radicals.
- b. Benzil dimethyl ketal. This is sold as Irgacure 651 (Ciba) and decomposes by a Norrish type 1 mechanism to produce free radicals.
- c. 2-hydroxy-2-methyl-1-phenyl-propan-1-one. Sold as Darocur 1173 by Ciba, this is an acetophenone derivative that decomposes by a Norrish type 1 mechanism to produce free radicals.
- d. Benzophenone. This compound and its substituted derivatives has been a popular initiator because of good deep section curing. It is used in combination with amines, especially tertiary alkyl amines, which act as hydrogen donors and lead to the generation of free radicals by a bimolecular Norrish type 2 mechanism.
- e. Phosphine oxides. Both acyl and biacylphosphine oxides are photoinitiators which, when used alone or in combination with other photoinitiators, absorb well into the visible part of the spectrum and are useful to cure highly pigmented systems. Irradiation leads to highly reactive phosphinoyl and phosphinyl radicals generated by a Norrish type 1 cleavage.

#### *4.5.1.2 Cationic Systems*

In principle, cationic systems should be the most versatile UV systems because of the wide range of monomers and oligomers that are theoretically available. In practice there are a limited number of commercially available monomers and oligomers and even fewer photoinitiators. Cationic systems are very fast curing and often cure to completion after irradiation is ceased. The major chemical limitations to photocationic systems are inhibition by atmospheric moisture and by small quantities of basic or alkaline materials.

##### *Monomers and Oligomers*

1. Epoxies – The epoxy monomers used in UV systems are called cycloaliphatic epoxies and are quite different from the monomers used in conventional epoxy resins. Typical examples are 3,4-epoxycyclohexylmethyl-3,4-epoxy-cyclohexane-carboxylate (Dow Chemical Cyacure 6100) and bis(3,4-epoxycyclohexyl) adipate (Cyacure 6199). These monomers are good for producing thin clear coatings but suffer from strong odours and post heating is often necessary to produce optimum properties.
2. Vinyl ethers – These monomers have been studied for many years by scientists in basic cationic polymerisation chemistry but until recently, few monomers were available which gave products with useful properties. ISP produces triethylene glycol divinyl ether and cyclohexyl vinyl ether. Morflex has a range of vinyl ether esters and urethane vinyl ether oligomers that are very attractive for producing fast curing, low odour systems with low toxicity.
3. Oxetanes – Toagosei in Japan have developed oxetane monomers. These 4-membered cyclic ether monomers are claimed to give superior properties to cycloaliphatic epoxies.

##### *Photoinitiators*

A limited number of photoinitiators are available for cationic systems. The most widely used are triaryl salts such as triphenyl sulfonium hexafluorophosphate (FX-512 from 3M) and mixed



triphenyl sulfonium salts (CyracureUVI-6974 and -6990 from Dow Chemical). These photoinitiators are decomposed by UV light by a homolytic cleavage to produce a radical anion and a radical cation. The radical cation abstracts hydrogen from surrounding molecules and generates a proton, which is the initiating species.

Ciba Specialty Chemicals have recently announced new iodonium salts for cationic curing, viz. 4-isobutylphenyl-4'-methylphenyliodonium hexafluorophosphate. Benefits are claimed to include high value in use, as the product is active at low concentrations and can be combined with thioxanthone photosensitisers.

#### **4.5.2 Benefits of UV Systems**

UV systems have the following advantages to the user:

- Speed of cure, often seconds – leads to increased productivity
- Energy savings – a fraction of the power consumption of heat curing
- Less stresses and movement than in heat cure
- Less floor space – small, compact curing systems
- Single component – no application of primers or mixing
- Reduced work in process – assembly to pack measured in minutes
- Safety – no hazardous solvents or other emissions

The primary limitation of UV systems is that the material to be cured must see suitable radiation. This means that in an adhesive application, one substrate must transmit appropriate UV or visible light. Also, assemblies with shaded areas will require a secondary cure mechanism.

#### **4.5.3 Advances in UV Technology**

##### **4.5.3.1 Shadow Curing**

One advance in UV systems is the ability to cure in so-called 'shadow areas', i.e., in the areas where UV light cannot penetrate. This is particularly important in complex assemblies such as in electronics where an adhesive might wick into small holes or gaps. This is usually achieved by heat curing, using a surface activator or incorporating some urethane chemistry in the systems, utilising free isocyanate groups to cure with atmospheric moisture. Dymax [8] have shown that atmospheric oxygen can be used to cure in the shadow areas by incorporating molecules with high levels of acryloxy functionality coupled with a metallic drier. Loctite have recently developed an interesting alternative type of system by making cyanoacrylate adhesives that also cure with UV radiation. This type of system combines the ability of cyanoacrylates to cure virtually instantly in small gap situations and also to cure by UV in exposed areas. This system will find many applications in rapid product assembly, such as in the medical device industry, but will be hindered by the inherently limited temperature and solvent resistance of cyanoacrylates.

##### **4.5.3.2 Minimising Shrinkage**

One of the goals of UV adhesive formulators is often to minimise shrinkage during curing so as to minimise stresses in assembled components. Dymax report the use of new acrylate functional cellulosic oligomers [9] that maximise crosslinking but minimise shrinking and are particularly suitable for bonding of precision optical assemblies.

Exfo Photonic Solutions have developed step-cure processes for minimising shrinkage during UV curing of adhesives

#### 4.5.3.3 UV Silicones

UV silicones are another type of free radical system. By combining their expertise in both acrylic and silicone chemistry, Henkel-Loctite has developed two types of proprietary silicones, one that cures upon exposure to UV only or silicones that cure partially upon exposure to UV light, followed by a secondary moisture cure mechanism that completes the cure and provides enhanced adhesion.

Both systems require high intensity UV light for curing. Like acrylics, UV silicones are inhibited by oxygen. The cured polymers provide outstanding low temperature flexibility, excellent electrical properties and a high degree of water resistance.

These are very high cost systems but prices are expected to fall with increased competition as basic patents expire.

It is not the intent of this report to cover UV curing equipment, save to say that a wide range of systems are available with various wavelengths and intensities with spot curing and flood systems being available. Articles on equipment and dispensers have appeared in recent issue of Adhesive and Sealants Industry Magazine [10, 11].

#### 4.5.4 Applications of Radiation Curing Adhesives

UV systems are used in wide range of industries and applications with some customers literally curing millions of parts per day – see Table 4.10.

<b>Table 4.10 Examples of UV adhesive and sealant applications</b>	
<b>Products /markets</b>	<b>Applications</b>
Circuit boards	Wire tacking
Electronic components	Pin attachments
Motors	Gasketing
Medical devices	Syringe assembly
Optical parts	Syringe needle assembly
Consumer glass repair	Surface mounting
Automotive mirrors	Gasketing
Auto windshield repair	Glass bonding
Display panels	Potting
Magnets	Encapsulation
Optical fibres	Bonding medical tubing
Video recorders	Tamper proofing
Disk drives	Die attach
Loudspeakers	Solder masks
Dental	Conformal coating repair

Radiation curing technology is confined to a limited portion of the adhesives industry. According to consulting company Kusumgar, Nerlfi & Gowney [12], the global consumption of radiation-cured adhesives in 2000 was 6000 tons worth \$370 million but most of this was used in dental procedures. The Freedonia Group estimated the non-dental market in 2000 at 2200 tons with a value of \$56 million [13].

UV cured adhesives and sealants have progressed from being a high technology alternative to other fastening systems to being indispensable materials in today's high tech society. Whilst it is difficult to predict huge growth potential in current applications in the future, growth should certainly be significant and steady as new applications open up, older technologies are replaced and costs come down with increased competition amongst suppliers.

Lamination applications are attractive new markets for UV adhesives and lamination of flexible packaging films and DVDs are forecast to be significant growth areas.

An alternative to using UV systems is to cure adhesives with high energy electron beams. Widely used in the coatings industry, electron beam systems do not need added photoinitiators and polymerisation is initiated by high energy electrons. Also electron beam systems do not require the substrates to be transparent as is the case for UV systems. The major factor that has limited electron beam curing in the adhesive industry has been the very high capital cost of the equipment, although there has recently been some market penetration in the film lamination and pressure sensitive tape industries.

#### **4.6 Solvent-Based Systems**

Solvent-based adhesives were traditionally attractive systems for both industrial users and consumers. They are low cost systems that dry quickly and frequently give high performance.

However, incidents of 'glue sniffing' and recognition of the health dangers and environmental impact of solvents have led to a decline in their usage. Most legislation to date has focussed on coatings and printing inks as the major source of volatile organic compounds (VOCs) but adhesives have been impacted dramatically as well.

Many industrial users have switched to water-based or 100% reactive adhesives and 'safe' consumer adhesives, based on water-based alternatives to solvent systems, have become prevalent.

However, some solvent-based adhesives are still the first choice in several applications. For example, despite considerable technical developments, many polychloroprene based contact cements still perform better in their solvent versions compared to latex versions. Nitrocellulose dissolved in acetone is still popular in the US consumer markets as Duco® cement (Devcon).

Some high tech medical device companies still use solvent cements for bonding of medical tubing, for performance and cost reasons.

It is expected that solvent based systems will continue to decline slowly as safer alternatives continue to be developed and worldwide legislation becomes stricter.

#### **4.7 Water-Based Systems**

Water-based adhesive systems are in fact some of the oldest adhesive systems known, many being based on natural animal or plant derived polymers.

The major driving force behind the development of water-based adhesives has been environmental pressures to eliminate hazardous and flammable solvents. Great strides have been made in raw material and formulations to give systems that will meet or exceed the performance of solvent-based systems. The wide range of available high-solids latex systems is the best example of this.

However, water-based systems have weaknesses:

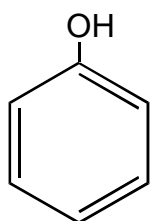
- They dry slower than most solvent systems
- Considerable energy is required for drying
- Around 50% of most latices is water, and the freight cost of shipping this much water is considerable

With regard to the freight issue, it is no coincidence that very large latex adhesives users and manufacturers are often located in close proximity, e.g., in the US, the area around Dalton, Georgia has the largest carpet manufacturers and several SBR emulsion producers.

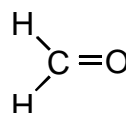
#### 4.7.1 Phenol-Formaldehyde and Amino Resins

##### 4.7.1.1 Phenolic Resins

Phenolic resins (PF) are made from the condensation of phenol and formaldehyde.



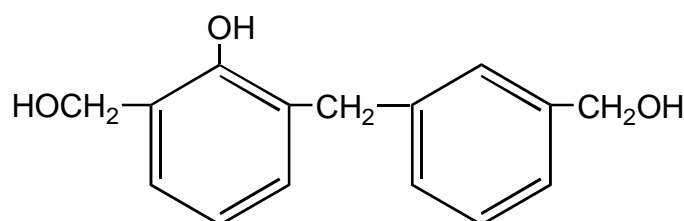
**phenol**



**formaldehyde**

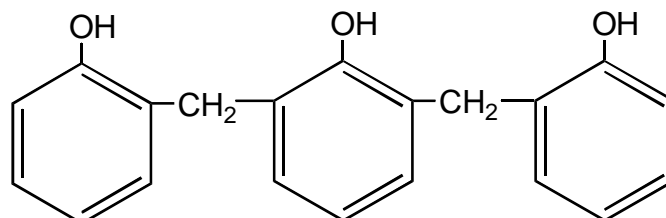
Bakelite, a crosslinking, thermosetting polymer was produced from formaldehyde and phenol and patented in 1909 by the Belgian chemist Dr. Leo Hendrik Baekeland. However, it was not until the 1930s that liquid resins suitable for adhesives were manufactured.

Although the chemistry of these reactions is quite complicated, two types of intermediates are generally produced, depending on the mole ratio of the reactants. Liquid resins called resols are formed when a mole excess of formaldehyde is used in the presence of a basic catalyst:



**resol**

Solid resins called novolacs are formed when an excess of formaldehyde is used in the presence of an acidic catalyst:



**novolac**

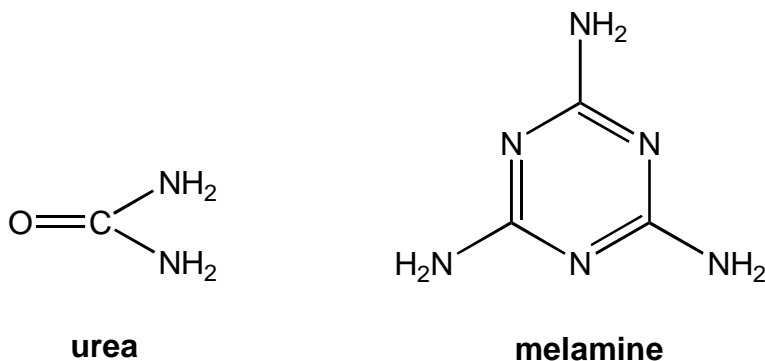
PF resins are low cost products with their major use being the bonding of exterior grade wood products, particularly in manufacturing plywood, particleboard and oriented strandboard (OSB). In plywood and particleboard production, resols are used either in liquid form or as a water-soluble powder. In OSB production, most plants use novolac resins in powder form.

Products made with phenol-formaldehyde, have proven to be more durable than wood when exposed to warm and humid environments, water, alternate wetting and drying, and even temperatures sufficiently high to char wood. These adhesives are entirely adequate for use in products that are exposed indefinitely to the weather.

Phenolic resins are also used as high temperature adhesives in the production of automotive disk brake pads and abrasive products.

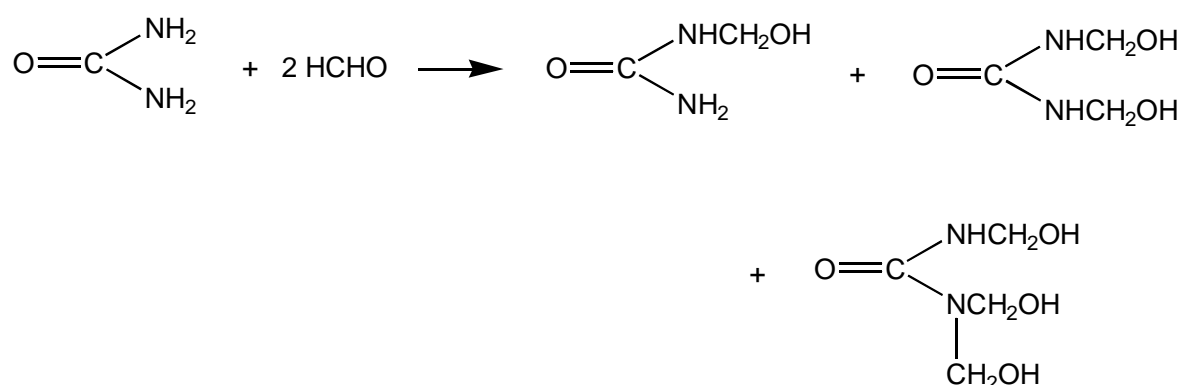
#### 4.7.1.2 Amino Resins

Amino resins are thermosetting polymers produced by the condensation reaction of formaldehyde and a compound containing amino groups. These amino groups are commonly found as amides in urea and melamine. The most important amino resins are urea-formaldehyde (UF) resin, melamine-formaldehyde (MF) resin and melamine-urea-formaldehyde (MUF) resin, which is a combination of the two resins. The latter may be either blends or copolymers of the two resins or UF resin fortified with melamine crystals (up to 20%). UF resins were commercialised in the 1930s and MF resins in the 1950s.



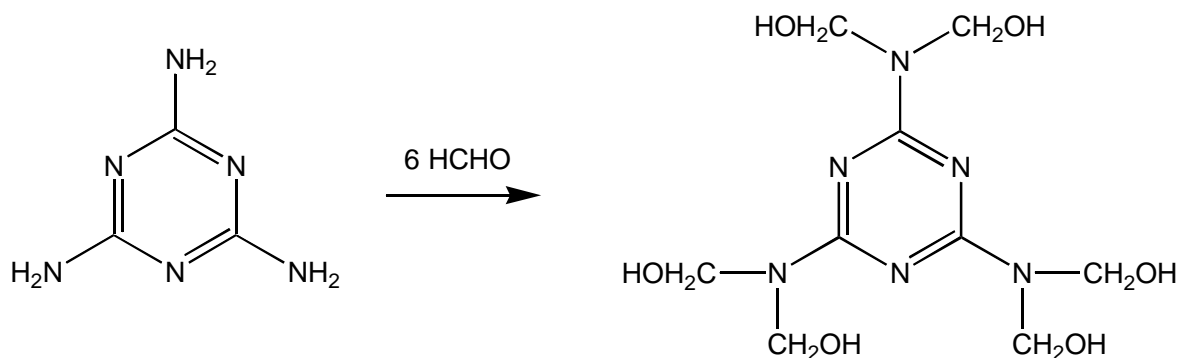
Both urea and melamine have many replaceable hydrogens and this multifunctionality makes these reactions even more complex than in PF resins.

Urea reacts with formaldehyde under alkaline conditions to produce mono-, di- and tri-methylolureas:



These condense under acid conditions, first to soluble resins and then to insoluble crosslinked resins.

Melamine can react with up to 6 moles of formaldehyde to produce a range of methylol compounds, e.g.:



These compounds then condense to form a highly crosslinked network, in a similar way as UF resins.

UF resins are relatively inexpensive to produce, light in colour and fast curing. However, wood products made with UF resins are susceptible to moisture and heat and are usually only used for interior applications.

MF resins are more expensive than UF but products made with MF are only slightly less durable than phenol-formaldehyde and still considered acceptable for exterior structural products.

Borden is the world's largest producer of formaldehyde and reports that the demand in formaldehyde adhesives in the construction and furniture industries is as shown in Table 4.11.

<b>Table 4.11 Markets for formaldehyde based adhesives</b>		
<b>Product type</b>	<b>% Adhesive volume used in:</b>	
	<b>Construction</b>	<b>Furniture</b>
Oriented strandboard	57	-
Plywood	20	4
Particleboard	15	71
Medium density fibreboard	8	25

In North America, Georgia Pacific, Borden and Neste combined control over 90% of the PF resin market for wood products.

In Europe, Borden, Neste and BASF are the three largest producers. Neste Chemicals and the chemicals activities of Dyno were recently merged to form the Nordkemi Group, mainly with the objective of becoming a global leader in resins and adhesives for the bonding and surfacing of wood products. In parallel with moves by speciality chemicals companies to target the wood products sector, vertically integrated producers of wood composites have emerged in Europe. One of the largest is Sonae Industria of Portugal, now a world leader in the wood panel sector. That company makes its own melamine, phenolic and formaldehyde resins.

Orica is the largest producer in Asia/Pacific, followed by Borden. Dyno also has a significant position in the Asian market. Mitsui Chemicals accounted for 30.8% of the UF resin adhesive production in 1999 in Japan. Other major producers in Japan include Honen Corp., with 18.5%; Oshika Shinko, with 15.4%; Sumitomo Bakelite, with 11.1% and Nippon Kasei Chemical, with 8.6%. Mitsui and Sumitomo Bakelite recently formed a joint-venture company, combining their wood adhesives operations.

Table 4.12 shows the demand for formaldehyde resins by region.

Table 4.12 Demand for formaldehyde resins (1000 tons)		
Region	PF	UF +MF
North America	1145	1038
Europe	1025	3444
Japan	37	305
China	113	957
Totals	2320	5592

#### 4.7.2 Latex (Emulsion) Adhesives and Sealants

Applications in adhesives and sealants comprise around 20% of all synthetic latex sales globally (this does not include non-woven, textile and carpet applications).

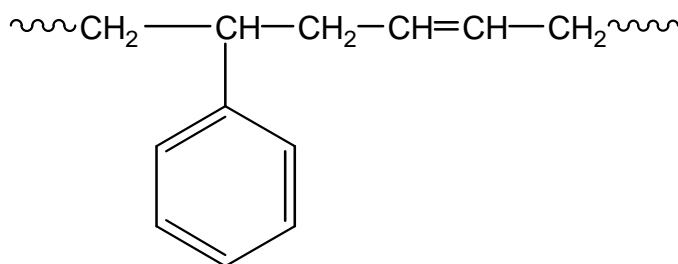
Natural rubber was the original latex polymer. Natural rubber co-exists with a range of synthetic rubbers, each of which has a defined position in the properties/price spectrum:

- Styrene-butadiene copolymers
- Acrylonitrile-butadiene copolymers
- Polychloroprene
- Acrylic polymers, including styrene acrylics and ethylene acrylics
- Vinyl acetate polymers
- Vinyl acetate-ethylene copolymers
- Vinyl chloride polymers and copolymers
- Polybutadiene
- Synthetic polyisoprene

A description of the major types of adhesive and sealant latices follows:

##### 4.7.2.1 Styrene-Butadiene Rubber (SBR)

SBR is a random copolymer produced by the copolymerisation of butadiene with styrene, either in emulsion or solution.

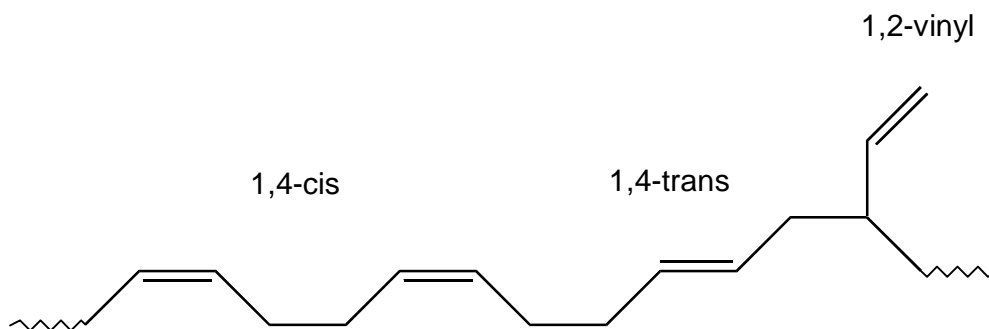


The most common styrene content is 23-25% for SBR used in the tyre industry but styrene contents of 50 to 70% are common in products for other applications.

Copolymers with more than 45% butadiene are sometimes referred to as SBR latex; products with more styrene may be referred to as SB latex.

Two main types of emulsion SBR are produced. ‘Hot’ rubber is produced by emulsion polymerisation at about 50 °C using persulfates as initiators. ‘Cold’ rubber is produced by emulsion polymerisation at about 5 °C using redox initiation.

It should be noted that butadiene monomer can be incorporated either by 1,4-addition, yielding the *cis* or *trans* stereoisomer, or by 1,2-addition yielding a pendant vinyl unit.



In SBR, the butadiene units have mixed stereoisomerism, typically consisting of about 20% cis-1,4-, 60% trans-1,4- and 20% 1,2-units, the exact composition being dependent of polymerisation temperature. Hot rubber contains branched molecules and macrogel, which whilst sometimes assisting processing, does yield vulcanisates with inferior properties.

Solid SBR elastomers are the largest-volume synthetic rubber, accounting for 41% of world consumption of synthetic rubber in 2000 (3.3 million tons). However, the percentage has been steadily declining for the past two decades (it was 57% in 1976) because of:

- (1) the increasing popularity of radial tyres, which use less SBR than other tyre designs (e.g., bias-belted tyres);
- (2) faster growth of other synthetic rubbers (e.g., EPDM, nitrile and polybutadiene rubbers), especially in non-tyre applications; and
- (3) severe price competition from natural rubber.

Modern manufacturing methods for SBR still use emulsion processes (known as E-SBR) but anionic polymerisation in solution using alkyl lithium catalysts (known as S-SBR) has become very important in recent years, particularly for tyre rubbers. S-SBR is a product that possesses a narrower and much more controllable molecular weight distribution than E-SBR and it is claimed that decreases in the rolling resistance of tyres of up to 20% can be achieved using S-SBR.

During the past ten years, North American E-SBR consumption decreased 10% as more S-SBR has been used to make these more fuel-efficient tyres.

In addition to SBR used in tyres, an additional 2.6 million tons of latex is used in liquid form, mainly in the form of high styrene content SB latex. Many SB latices are carboxylated by the use of co-monomer unsaturated acids such as maleic, fumaric, acrylic or methacrylic (these copolymers are often referred to as X-SBR). Carboxylation generally leads to enhanced adhesive properties and gives alternative methods of crosslinking.

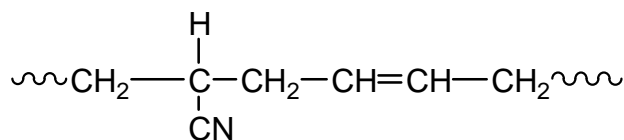
The main applications for SBR latex in the adhesives and sealants industry are for bonding tufted carpets, for bonding non-woven fabrics as adhesive/sealants in the construction industry and as pressure-sensitive adhesives (PSAs).

There are many worldwide producers of SBR latex, but BASF and Dow Reichhold have by far the leading market shares. There is significant over capacity for SBR emulsions globally but this is expected to decrease as more new rubber is made by solution processes.

#### 4.7.2.2 Acrylonitrile-Butadiene Copolymers (NBR Latex)

Commonly called 'Nitrile', these elastomers are copolymers of acrylonitrile and butadiene. They are produced by emulsion polymerisation in batch or continuous processes.





Similar to SBR, the butadiene unit may be incorporated in the *cis*-1,4-, *trans*-1,4- and 1,2-vinyl configuration, where the vinyl is favoured by increasing the polymerisation temperature.

Many nitrile latices are actually terpolymers of acrylonitrile, butadiene and methacrylic acid and known as carboxylated NBR latices (commonly referred to as X-NBR). Methacrylic content is typically 3-6%, with butadiene at 55-70% and acrylonitrile at 25-50%.

Nitrile rubber latices give products that exhibit excellent resistance to solvents, fuels, oils and greases, are abrasion resistant, bond to a wide variety of substrates and exhibit a high degree of toughness.

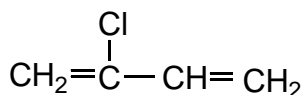
Nitrile latices are used as textile and non-woven adhesive binders, including the manufacture of synthetic leather.

Other applications include blending with phenolic and epoxy resin emulsions for adhesive and sealant applications.

Manufacturers of nitrile latices are BASF, PolymerLatex, Dow Reichhold, Zeon, Noveon and Synthomer.

#### 4.7.2.3 Polychloroprene (CR)

Polychloroprene is the linear polymer of chloroprene (2-chloro-1,3-butadiene).



#### Chloroprene

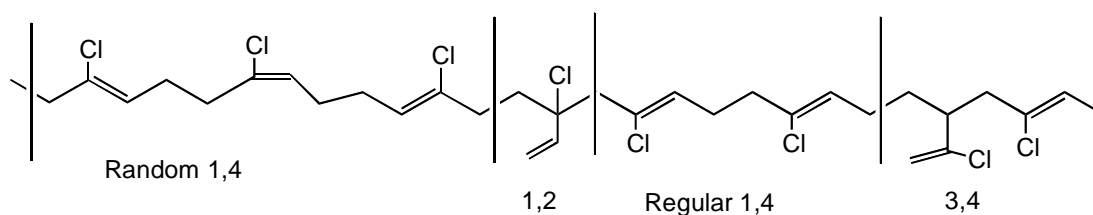
It was invented by DuPont in 1931 and was the first synthetic rubber with similar elastic properties to natural rubber. Although use of this rubber has declined somewhat in recent years due to competition from other elastomers and resistance of some countries and customers to the use of chlorinated materials, it remains as a very significant synthetic elastomer.

Modern manufacturing methods derive chloroprene monomer from the chlorination of butadiene.

Polychloroprene is made by a free-radical emulsion polymerisation, either in a batch or a continuous system.

Polychloroprene latices have particle sizes <200 nm and are made alkaline to counteract any drop in pH on storage due to acid generation by dehydrochlorination.

Polychloroprene consists of four different structural units, stereoisomers *cis*-1,4 and *trans*-1,4, 3,4 and 1,2. The 1,2 units exist at about 1.5% in the polymer and are the primary sites for crosslinking of the elastomer.



In practice the polymer has a very high *trans*-1,4 content and this regular structure allows ready crystallisation of the rubber.

Crystallisation is very important in the use of polychloroprene in adhesives. Fast crystallising polymers give very rapid strength build up but tend to be somewhat brittle and have low autoadhesion. In practice, a compromise between these properties has to be achieved. The crystallisation in the adhesive disappears on heating and this property is used to prepare heat-activated contact adhesives.

Slow crystallising grades can be made by using 2,3-dichloro-1,3-butadiene as a comonomer. This comonomer reduces the degree of crystallisation by introducing irregularities into the polymer chain. Crystallisation resistant grades are used to produce rubber articles or adhesives that have to retain their rubbery properties at very low temperatures. Other comonomers can also be used, including carboxylic acids such as methacrylic acid, which give carboxylate pendant groups that can be crosslinked with metal salts.

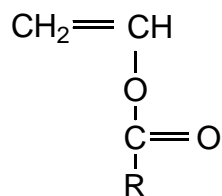
The major applications for polychloroprene latices are in contact adhesives.

Global production of polychloroprene latex is estimated at 20,000 tons. There has been considerable consolidation of manufacturers and plants in recent years with DuPont Dow Elastomers being the only manufacturer in North America with Polimeri Europa (Enichem) and Bayer, the only ones in Europe. Japanese producers are Denki Kagaku Kogyo, Tosoh and Showa DDE.

In 2001, polychloroprene products made by DuPont Dow Elastomers, formerly designated as Neoprene 'Latex' became known as Neoprene 'Liquid Dispersion'. This was a name change only made to differentiate DuPont Dow's water-based products from the natural latex products coming under increasing scrutiny around the world, especially in medical and industrial glove applications.

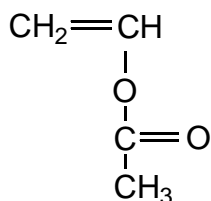
#### 4.7.2.4 Vinyl Ester Polymers

Vinyl esters are esters of monocarboxylic acids:

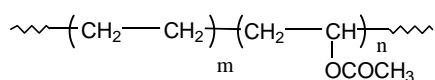


where R is an alkyl group.

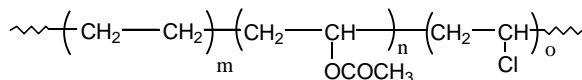
The most common and largest volume commercial product is vinyl acetate:



Vinyl ester latices include vinyl acetate polymers (VA) and several random copolymers, e.g.:



**Vinyl acetate-ethylene**



**Vinyl acetate-vinyl chloride-ethylene**

Vinyl acetate-acrylate copolymers can also be made and are called vinyl acrylics.

Vinyl acetate homopolymers and copolymers are manufactured by free radical emulsion polymerisation.

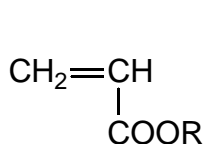
Copolymers of vinyl acetate with ethylene were developed as a way of plasticising polyvinyl acetate without the need for external plasticiser and these resins have become quite important in adhesives. Other monomers such as alkylacrylates, alkylmaleates, alkylfumarates and ethylene can be copolymerised with vinyl acetate. However, ethylene is a much more effective plasticiser for polyvinyl acetate than maleate and acrylate comonomers, since smaller amounts of ethylene are necessary to achieve equivalent decreases of the T<sub>g</sub> of polyvinyl acetate. This is because acrylate and maleate comonomers plasticise polyvinyl acetate by introducing bulky groups to the polymer chain, thus achieving flexibility by physically separating polymer chains from each other. Ethylene works by eliminating acetate groups from the chain, which results in the actual flexibilising of the polymer backbone.

The largest single market for VA homopolymer and copolymer emulsions is adhesive applications, offering low cost systems with very fast adhesive build-up on many surfaces, particularly paper and wood substrates.

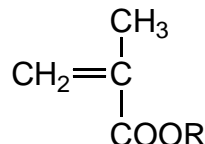
National Starch and Air Products Polymers are the leading manufacturers of vinyl acetate emulsions. Air Products Polymers is the global market leader in vinyl acetate-ethylene emulsions with Clariant holding the leading share in Europe.

#### 4.7.2.5 Acrylic Polymers, Including Vinyl Acrylics and Styrene Acrylics

Acrylics are homopolymers and copolymers of acrylic and methacrylic monomers.



**acrylate monomer**



**methacrylate monomer**

They are the most versatile of the synthetic latices, because of the wide range of monomers and comonomers available, however, their relatively high cost, compared to vinyl esters has limited their market penetration somewhat.

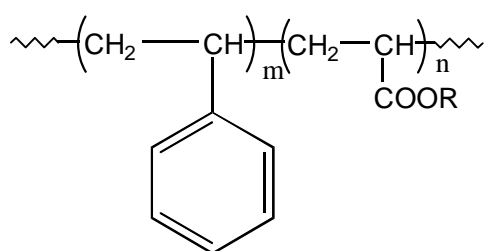
They are manufactured by free radical emulsion polymerisation using batch or semi-batch processes. There are numerous monomer combinations to produce copolymers or terpolymers or higher combinations, leading to a very large number of possible variations in final properties.

Typical monomers include; acrylates such as methyl acrylate, ethyl acrylate, *n*-butyl acrylate, *t*-butyl acrylate, 2-ethyl hexyl acrylate; and methacrylates such as methyl methacrylate and butyl methacrylate.

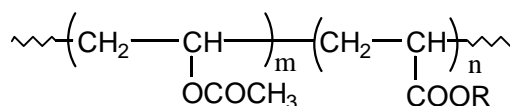
Furthermore, by incorporating monomers with functional groups, a variety of crosslinking reactions can be used with acrylic latices. There are two-component crosslinking systems where one of the crosslinking components is added just before application of the latex. Alternatively there are self-crosslinking (single-component) systems where all reactive components are present and long-term storage stable. The crosslinking reaction can be triggered by the evaporation of water upon drying, a change of pH, or by curing at elevated temperature.

Examples of suitable crosslinking systems are the reaction of aziridines with acid groups on the polymer backbone, the reaction of hydroxyl functionality on the backbone with post added isocyanates or melamines, the reaction of amines with epoxy functionality where either can be on the polymer backbone, the auto-oxidation of incorporated fatty acid groups, the self condensation of alkoxy-silane functionality, the self condensation of *n*-methyllolacrylamide, metal-ion co-ordination with backbone functional groups such as acetoacetoxy groups or acid groups, and the reaction of acetoacetoxy groups with amines or acetoacetoxy groups with unsaturated groups in a Michael reaction.

Less expensive latices can be prepared by using copolymers of acrylics with styrene, known as styrene acrylics and with vinyl acetate, called vinyl acrylics.



**styrene acrylic**



**vinyl acrylic**

Styrene acrylics in particular have become successful as low cost resins, with some advantages including good moisture resistance. The most popular latex is based on styrene and butyl acrylate.

Acrylic latices are the fastest growing category of adhesives latices and are low cost alternatives to polyurethanes in many flexible packaging applications. They are also one of the leading technologies for producing high performance pressure-sensitive adhesives and high performance sealants.

BASF is the leading global producer of acrylic emulsions. Rohm and Haas and Dow Chemical are also major suppliers.

#### 4.7.2.6 Ethylene-Vinyl Chloride Copolymers (EVCL)

Vinyl chloride and ethylene can be copolymerised by free radical emulsion polymerisation at high pressures to produce ethylene-vinyl chloride copolymers (EVCL). Variations include a third monomer such as vinyl acetate or monomers with pendant carboxyl or amide groups. These halogen-containing polymers are particularly suitable as flame retardant adhesives for bonding and coating fabrics.

Air Products and Chemicals is the leading supplier of these emulsions.

#### 4.7.2.7 Polybutadiene

Polybutadiene was first manufactured in Russia and Germany in the 1920s by polymerising butadiene with sodium and called 'Buna' rubber. Today most polybutadiene is produced in solution with alkyl lithium catalyst and is used in tyre production.

Latices of polybutadiene are still manufactured and used in adhesives.

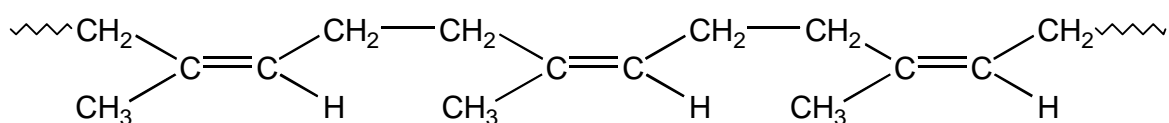
Polybutadiene is a very tacky polymer with a very low T<sub>g</sub> of -79 °C and latices are used for manufacturing low temperature tape and label pressure sensitive adhesives. They are also used as heat curable adhesive/sealants in the automotive industry

The Sartomer Company has developed methods for preparing emulsions from solid maleinised polybutadiene, which have very good adhesive properties, particularly in bonding textiles to rubbers.

#### 4.7.2.8 Natural Rubber

Natural rubber latex contains polyisoprene (IR) and is produced by the *Hevea Brasiliensis* tree, which is grown on both smallholdings and large plantations in East Asia. It is harvested by tapping the trees and then concentrating the latex.

Diene monomers like isoprene can polymerise in various ways to produce several repeating units, viz. 1,2-IR, 3,4-IR and the two stereo isomers, *cis*-1,4 IR and *trans*-1,4 IR.



***cis*-1,4 polyisoprene**

The major component of natural rubber (99%) is *cis*-1,4 polyisoprene.

Natural latex is used quite widely as a contact cement and as a so-called 'cold adhesive' in packaging. Natural latex has a property known as 'autoadhesion', which means that materials can be coated with adhesive, allowed to dry, and then combined under light to moderate pressure. This results in an instant bond without any heating step. This is very useful for packaging snack foods and foods that can't be exposed to heat such as chocolate or ice cream.

#### 4.7.2.9 Applications for Latices

Packaging is the largest single market for latex adhesives with over 50% of latex used in this market segment. The largest application is packaging adhesives used for rigid packaging applications like paper and paperboard packaging, including boxes and folded cartons. Vinyl acetate, vinyl acetate-ethylene and SBR emulsions are the major types used for these applications.

Label and tape applications for both liquid and pressure sensitive adhesives are also major applications and acrylics are very important raw materials in these products. Emulsions compete with other environmentally acceptable technologies for these applications, particularly hot melt adhesives.

Although water-based emulsion adhesives have been used for many years in flexible packaging applications like paper bags and sacks, they are becoming increasingly important in packaging applications for laminating plastics and foils. Adhesives play an integral role in the production of this flexible packaging. The main function is to bond two or more substrates together to form a lamination having more useful properties than the sum of its parts. Adhesives, although usually only a small portion of the entire lamination when compared to the wide range of films, foils, papers or printing inks used in flexible packaging, are vital for maintaining the end use properties of a finished package. Adhesives are generally applied in one of the last steps of the converting process and are often given the task of overcoming inherent shortcomings of the other flexible packaging materials. Acrylic emulsions are the basis of adhesives in this area and are proving to be cost-effective alternatives to one-part and two-part polyurethanes.

The largest single application for SBR latex is in the manufacturing of tufted carpets.

Latex adhesives are important in furniture manufacturing including edge banding, panel bonding and application of veneers. Polyvinyl acetate and crosslinkable acrylics are the major adhesive bases and compete with high performance hot melts for many applications.

Latices, particularly SBR and vinyl acetate, are also major raw materials in the production of construction adhesives, household glues and DIY woodworking glues. Acrylics are used widely in consumer and professional caulks and sealants because of their excellent water resistance.

Other latices also find applications in adhesives, for example, polychloroprene is used in contact adhesives for furniture, kitchen cabinets, custom display cabinets, interior and exterior panels and partitions, footwear, automotive trim, roofing membrane attachment, and a wide variety of related applications where quick, high strength permanent bonds are needed. In contact adhesives polychloroprene has a similar property as natural rubber, viz. autoadhesion. The bond strength of the assembled components is often sufficient to enable additional finishing operations without clamping or fixturing.

The worldwide market for latex used in adhesives and sealants is close to 3 million tons.

#### **4.7.3 Synthetic Polymer Solutions**

There are several water soluble polymers that can function as adhesives. Examples are polyvinyl alcohol and polyvinyl pyrrolidone. Polyvinyl alcohol solutions make excellent consumer paper glues. Gelled water solutions of polyvinyl pyrrolidone are the basis in the well-known glue sticks, e.g., the Pritt® glue stick from Henkel Corporation.

One of the problems with water-based adhesives is that they are moisture sensitive. This weakness can be overcome by using, for example, acrylic polymers with a high carboxy functionality that can be dissolved in water with the addition of bases such as ammonia or triethanolamine. The base evaporates on drying to give a water resistant system.

Sometimes, water sensitivity can be beneficial. For example, temporary adhesives (called ‘basting adhesives’) are used to hem fabrics prior to stitching and the adhesives dissolve when the fabrics are subsequently washed.

#### **4.7.4 Casein Adhesives**

Casein adhesives are very old products that were originally developed by Borden Chemicals Inc. from the by-product remaining after their invention of condensed milk manufacturing, which was produced to supply fresh milk to the troops of the American Civil War. This, once waste by-product, was quickly developed and became an industry standard adhesive from the 1860s until about 1930.

Casein adhesive is prepared from casein curd, which is precipitated from skim milk or buttermilk either by allowing the milk to sour naturally, or by adding acid to it.

To make the adhesive, the curds are dissolved in alkaline water such as limewater to which other chemicals such as formaldehyde or copper chloride are added. Most casein adhesive is sold as a dry powder and must be mixed with water before it can be used. Once mixed with water, it has a relatively short pot life. Pot life can be increased but only at the expense of moisture resistance. Until the introduction of adhesives based on synthetic resins, casein glues were very important in wood bonding because of their superior moisture resistance, but have been replaced by phenolic and amino resins.

Casein adhesives had several characteristics that limited their usefulness. They tended to stain those species of wood that are rich in tannic acid such as the oaks, which largely excluded them from the furniture industry.

Casein adhesives are still quite important in the labelling of glass containers such as beverage bottles, preserve jars and other containers. They can be applied to wet or dry, cold or hot surfaces and can easily be removed by cleaning machines.

#### **4.7.5 Starch Adhesives**

Starch is a natural polysaccharide product and is found in almost every plant.

The principal sources of most commercial starches are maize, potato, tapioca and wheat. Starch adhesives are low cost products that are used widely in high volume applications, particularly to bond paper based products.

The largest single application for starch adhesives is in the manufacture of corrugated boxes. Most starch based corrugated adhesives are based on the Stein Hall process invented and patented in the 1930s.

Every corrugated box plant prepares some form of starch based corrugating adhesive to bond the fluted liners and medium together. Each box plant has a formula created for their specific needs, including type of machine, product mix, special needs (e.g., water resistance) and converting requirements. The industry still uses old jargon, for example ‘cooking’ of starches and ‘glue kitchens’.

The adhesives are typically 25% solids, and are applied to the top of the flutes by glue applicators and then dried by a combination of heating, absorption into the board and evaporation.

The objective in a corrugating plant is to produce a reliable, consistent bond at the highest possible line speeds. An adhesive needs to have the correct rheology to be coated quickly, have sufficient wet tack to hold the flutes and medium together, penetrate the board for maximum adhesion, then gel and dry at the lowest temperature possible to maximise line speed and minimise use of energy.

A typical starch adhesive has the following ingredients:

- Raw starch – commonly called pearl starch, builds the bulk of the solids and absorbs water rapidly to form the main part of the glue line.
- Carrier starch – this is called ‘cooked’ starch that is gelatinised by heating with caustic soda and suspends the raw starch. It also influences the viscosity of the adhesive and provides wet-tack.

- Borax – gives rapid swelling of the raw starch and reacts with the carrier starch to modify the rheology of the adhesive and control the gel point.
- Sodium hydroxide – reduces the temperature of gelation of the raw starch, allowing bond formation at lower temperatures and faster line speeds. Also assists penetration of adhesive into the paper and, with borax, controls the rheology of the adhesive.
- Water – is a transport medium and necessary for swelling of the starch.
- Additives – various materials are added to adjust bonding speed, such as polyvinyl alcohol. Starch is not water resistant and other resins are added to enhance moisture resistance. Additives are also necessary for the control of bacteria, yeast and mould infection.

Due to changes in paper and the increased use of smaller flutes in corrugated in recent years, continuous adhesive development is taking place. Some newer adhesives avoid the use of carrier starches and are particularly effective on heavy walled board.

A variation on common starch adhesive is dextrin adhesives. Dextrin is a water-soluble lower-molecular weight polysaccharide produced by the treatment of starch with heat and strong acids.

Another major application for starch and dextrin is in adhesives for envelopes. The re-moistenable adhesive on the sealing flap and the seam adhesives are typically dextrin-based or a blend with PVA emulsion.

Starch was the main type of adhesive used traditionally for wallpaper adhesives, although with the advent of new wallpaper materials such as vinyl and the change in walls such as using 'drywall' (paper-faced gypsum), many modern adhesives use different adhesives based on cellulosic polymers such as methylcellulose, carboxymethyl cellulose and sodium carboxymethyl cellulose.

Starch based adhesives are also used in the following applications:

- Paper bags
- Paper boxes
- Carton sealing
- Case sealing
- Tube winding
- Labels for glass bottles
- Laminated paper board
- Gummed tape
- Gummed paper

The global market for starch-based adhesives is around 5 million tons with a value of \$2.2 billion.

Important suppliers of starch for adhesives include National Starch (US) and Cerestar (France).

#### **4.8 Inorganic Adhesives**

Inorganic adhesives are used for a wide range of applications, ranging from bonding of paper to high tech applications.

Sodium silicate is the oldest inorganic adhesive and is the generic name for a series of compounds derived from soluble sodium silicate glasses. These are water solutions of sodium oxide ( $\text{Na}_2\text{O}$ ) and silica ( $\text{SiO}_2$ ). Varying the ratio of  $\text{SiO}_2:\text{Na}_2\text{O}$  and the total solids content results in solutions that have different adhesive properties.



Soluble sodium silicates are produced by two methods; one way is by fusing sand with alkali (soda ash) to produce a silicate glass. This glass is then dissolved under autoclave conditions to produce silicate liquor. The other method is to produce silicate liquor directly by the dissolution of sand in sodium hydroxide.

Sodium silicates are versatile and economical adhesives. They are an alternative to starches for the bonding of corrugated containers, but for high volume production they suffer from the disadvantage of running at much lower line speeds than starches, being quite corrosive to machinery and making the board more difficult to recycle. They tend to be used for speciality applications such as:

- Paper tubes and cores
- Fibre drums
- Cornerboard, angleboard
- Paperboard laminates
- Paper/metal foil laminate

One of the important uses for inorganic adhesives is for high temperature applications, particularly in bonding ceramics and ceramics to metals. In contrast to organic adhesives where few can perform above 250 °C, ceramic adhesives have been developed which offer a service temperature of over 2000 °C.

These are based on inorganic binding compounds such as sodium silicates and various metal phosphates, with carbon, alumina, silica, magnesia or zirconia powder fillers. Ceramic adhesives can be formulated into one-part or two-part systems and are often supplied as a water-based binder solution and ceramic filler, which are mixed into a slurry for application as adhesives or sealants. Suitable selection of the binder and, more importantly, the filler, allows the coefficient of thermal expansion of the adhesive to be matched to that of a substrate to minimise stresses during heating and cooling.

One-component adhesives will cure slowly by drying or can be heated to speed up the process. Versions where cure is accelerated by atmospheric moisture are also available.

These adhesives can also be prime candidates where low electrical conductivity but high thermal conductivity is important.

Table 4.13 shows typical applications for inorganic ceramic adhesives. This list was derived from Sauereisen ([www.sauereisen.com](http://www.sauereisen.com)).

<b>Table 4.13 Typical applications for inorganic ceramic adhesives</b>	
<b>Infrared radiant heaters</b> – adhesion of heating coil to various substrates	<b>Lighting/lamps</b> – potting of bulbs into lamp housing
<b>Igniter tip assembly</b> – adhesion of igniter tip to ceramic	<b>Resistors</b> – encapsulation of resistor wiring
<b>Circuit breakers</b> – cementing metal contact leads	<b>Furnace maintenance</b> – lining for surface of furnace door and walls
<b>Sensors</b> – bonding glass to metal alloys	<b>Thermocouples</b> – assembly of thermocouple components
<b>High temperature filters</b> – adhesion of filter to metal housings	<b>Igniters</b> – bonding and potting of ferrous or nonferrous elements into ceramic substrates
<b>Resistors</b> – potting of resistor in ceramic housing	<b>Heating elements</b> – potting elements into a base

Weaknesses of inorganic adhesives include brittleness, sensitivity to moisture, and often lower adhesive strength than their organic counterparts.

#### 4.9 Pressure Sensitive Adhesives

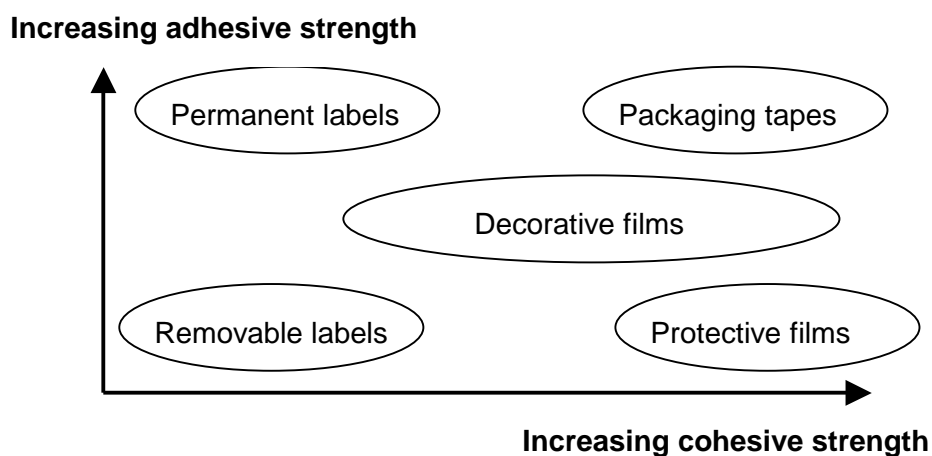
The first pressure sensitive adhesive (PSA) was probably invented in 1882 when Paul Beiersdorf patented prepared mixtures of rubber and sticky resins, zinc oxide and medicine, applied it to a linen backing and used it to treat skin ailments. The modern self-adhesive label industry started in 1935, when R. Stanton Avery produced the first coating unit to apply adhesive to a paper roll.

Pressure sensitives are defined as adhesives that when dried or fully cured are permanently tacky and will adhere to surfaces by the application of pressure. They can be supplied as liquids or bought in finished form as labels, tapes and films. The ‘tack’ of a PSA enables it to adhere to a surface under light pressure with minimum contact time. PSAs are not liquids but they are soft thermoplastics that flow and wet a surface at room temperature. The pressure applied ensures good wetting of the surfaces. PSAs, in contrast to adhesives that cure to solids, continue to flow after application and bond strengths tend to increase over time.

The balance between adhesive strength and cohesive strength of the adhesive determines the suitability of a PSA for a particular application (see Figure 4.3).

Adhesive strength is a measure of the molecular force of attraction or bond between the adhesive and the surface it contacts.

Cohesive strength is the internal strength of an adhesive and its ability to resist failure or slippage from external shear forces.



**Figure 4.3 Relationship between adhesive and cohesive strength for various PSA products**

Thus a PSA for a permanent label only needs good adhesive strength under the conditions of use, whereas a packaging tape, which can be under stress and exposed to high temperatures needs both high adhesive and cohesive strength. A PSA for protective film needs good cohesive strength but the adhesive strength should remain low to enable the film to be removed without leaving adhesive residue on the surface.

PSA products are different from other adhesives in that the adhesive manufacturer or converter does all the application and curing. The end user only has to take a tape, label or roll and put it in place without having to handle hazardous liquids or application and curing equipment.

Most base polymers for PSA adhesives have very low Tgs from  $-60^{\circ}\text{C}$  to  $10^{\circ}\text{C}$ . Examples are:

- Natural rubber
- Styrene-butadiene rubber
- Styrene-butadiene-styrene block copolymers
- Styrene-isoprene-styrene block copolymers
- Polyisobutylene
- Ethylene-vinyl acetate copolymers
- Ethylene-vinyl-acrylic terpolymers
- Polyvinyl ethers
- Acrylic ester copolymers
- Silicones

PSAs are manufactured using solvent-based, hot-melt, UV and emulsion processes. However, manufacturers have been moving rapidly away from solvent-based systems towards more environmentally acceptable technologies. UV cured and hot melt PSAs can be processed very quickly because no solvents or water need to be removed.

Hot melt PSAs are usually based on styrene-butadiene-styrene (SBS) or styrene-isoprene-styrene (SIS) block copolymers. These so-called thermoplastic elastomers are elastomeric solids at room temperature but start to flow at 90-100 °C (the T<sub>g</sub> of polystyrene). However, these adhesives have very poor heat resistance and poor resistance to solvents or the plasticisers in materials like flexible PVC. It has been shown that crosslinking these types of polymers with UV or chemical means can dramatically improve their performance [14].

UV PSAs are formulated from acrylic monomers and oligomers with added rosin tackifiers, diluents and a photoinitiator. They cure almost instantaneously under UV radiation. However, their high costs have limited market penetration. Versions of UV PSAs that can be applied as hot melts have also been developed [15]. These are based on acrylic polymers [16], poly (ethylene-butylene) diblock copolymers terminated with epoxy and hydroxy groups [17], styrene-butadiene-styrene triblock copolymers with pendant vinyl groups on the butadiene block [18] or acrylate-polyester-acrylate block copolymers [19].

The most versatile method for preparing PSAs is emulsion polymerisation, with the inherent disadvantage that a considerable amount of energy is required to dry the adhesives. The main classes of emulsion pressure-sensitive adhesives are styrene-butadiene rubber (SBR), ethylene-vinyl acetate (EVA) and acrylics. As is the case for solvent-based SBR adhesives, SBR emulsion requires formulation with a tackifying resin to obtain pressure-sensitive properties. In contrast, EVAs and acrylics can be made to be inherently pressure sensitive through the choice of monomer mix, molecular weight and crosslinking during the polymerisation process. However, tackifiers such as rosins can enhance their pressure sensitive properties. Some 360,000 tons of emulsion polymers are currently used to produce tapes and labels, forecast to increase to 400,000 tons by 2006 [20].

PSAs can be formulated with a wide range of adhesive and cohesive properties. Tackified rubber based adhesives show excellent peel adhesion to many substrates, but they perform poorly at elevated temperatures. Acrylic based adhesives, in contrast, either have outstanding peel adhesion and poor elevated temperature performance or low peel adhesion and outstanding elevated temperature performance.

Avery Dennison has shown that dual-cure adhesives can be prepared with both good peel adhesion to a variety of substrates and a high shear adhesion failure temperature [21]. This was achieved using a tackified acrylic polymer containing co-monomers with glycidyl and carboxy functionality. Initial curing of the adhesive by heat or UV yields an adhesive with excellent tack and peel and a good balance of high temperature shear. Secondary curing at higher temperatures such as may be experienced in use of the adhesive appear to give inter-chain crosslinking of the glycidyl and carboxy groups to yield structural polymers.

PSAs are supplied as single sided tapes, labels and films, double sided tapes and transfer films where the adhesive is applied to a release liner and transferred from this to the surface being bonded.

PSAs are used for a wide range of applications in many industries (Table 4.14).

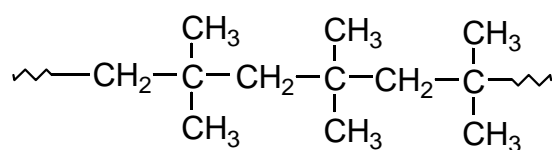
Table 4.14 Applications for pressure sensitive adhesives		
Paper labels	Adhesive bandages	Postage stamps
Film labels	First aid tapes	Envelopes
Packaging tapes	Surgical tapes	Note pads
Office tapes	Transdermal patches	Floor tiles
Home tapes	Nameplates	Window films
Masking tapes	Advertising signs	Protective films
Electrical tapes	Traffic signs	Decorative films
Baby diaper tapes	Vehicle signs	Abrasive disks
Medical tapes	Automotive labels	Membrane switches
Foam sealing tapes	Automotive adhesives	
Duct tape		

PSAs, because of their convenience, are growing rapidly in applications worldwide. For example, the market research firm, Frost and Sullivan have reported that five billion square metres of tapes were produced in Europe last year. Around 70% were packaging tapes, 16% speciality tapes, 9% masking tapes, and 5% consumer and office tapes. At the same time, 3.8 billion square metres of labels were produced, with the stock label market being dominated by paper rolls (74%), followed by non-paper rolls (17%), paper sheets (7%), and non-paper sheets (3%).

Over 40 billion self-adhesive stamps are used per year in the US, equating to around 26,000 square metres of pressure sensitive adhesive.

#### 4.10 Butyls

Butyl sealants are the generic name for polymers of isobutylene known simply as polyisobutylene (PIB) for the homopolymer, or butyl rubber, which is a copolymer of isobutylene containing 1 to 3% of isoprene. The isoprene acts as a crosslinking site.



**polyisobutylene**

Chlorobutyl or bromobutyl rubbers can also be made with the chlorine and bromine atoms being alternative crosslinking sites.

Butyl polymers were originally prepared by the Standard Oil Company in the 1920s and 1930s and are the most successful commercial application of cationic polymerisation. The polymers are prepared by low temperature polymerisation using Friedel-Craft halide catalysts.

Butyl is a hydrocarbon polymer with outstanding resistance to water and has very low air and moisture vapour transmission rates. An early use was in the manufacture of inner tubes for tyres. PIB has a very low Tg of  $-60\text{ }^{\circ}\text{C}$ , which gives flexibility even at very low temperatures.

Sealant formulations are normally prepared by mixing butyl polymer with various levels of both low and high molecular weight PIB to modify properties.

Butyl sealants are available in three general forms:

- Pumpable liquid sealants
- Hot applied sealants
- Sealant tapes.

Pumpable sealants are non-crosslinked systems that can be dispensed from cartridges or dispensing systems and because of the high molecular weight of most butyls, must be cut with solvents to aid in dispensing. High levels of fillers (typically calcium carbonate) are also often used. These sealants are good general purpose sealants used in construction applications but suffer from shrinkage on drying and limited joint-movement capability. Typical uses include sealing curtain wall joints, bedding thresholds, and where a seal is required for preformed gaskets.

Table 4.15 shows the strengths and weaknesses of butyls.

<b>Table 4.15 Advantages and disadvantages of butyl sealants</b>	
<b>Advantages</b>	<b>Disadvantages</b>
Easy to use – one-component Good adhesion to most surfaces Very low MVTR <sup>1</sup> Very flexible at low temperatures Good weathering ability Good electrical insulators	Poor gap filling for liquid versions Medium JMC <sup>2</sup> High shrinkage due to solvent evaporation
<sup>1</sup> MVTR = moisture vapour transmission rate <sup>2</sup> JMC = joint movement capability	

Butyl rubber has the lowest moisture vapour transmission rate of all elastomers and is used widely as the primary seal in double glazing applications and to seal dry cell batteries. Polyisobutylene also finds uses in pressure sensitive adhesives, particularly for electrical tapes.

Exxon, BASF and Bayer are the major suppliers of butyl polymers.

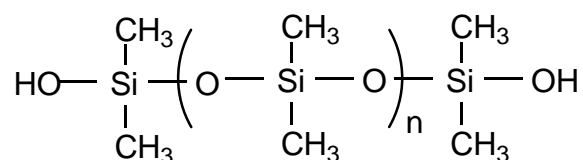
#### 4.11 Silicones

Silicone sealants are based on polymers containing alternating oxygen and silicon atoms in their backbones with various organic groups in their side chains. Their unique properties are derived from this marriage of an inorganic Si-O-Si backbone (which comes ultimately from silica) and organic side chains.

The basic work on silane chemistry that led to silicones was started back in the late 19<sup>th</sup> Century by Frederick Kipping and others in Europe, but the real development of silicone elastomers was done in the industrial laboratories of Corning Glassworks (later Dow Corning) and General Electric.

Although the term silicone encompasses a wide range of materials, ranging from oils and fluids to gels and solid rubbers, we are concerned here with liquid silicones that can be cured into solid rubbers to fulfill a sealing capacity.

Most silicone sealants are based on silanol-terminated polydimethyl siloxanes, often called silanols, e.g.:



where n is typically 300 to 1600

Silicone polymers can be formed in two ways from these silanols:

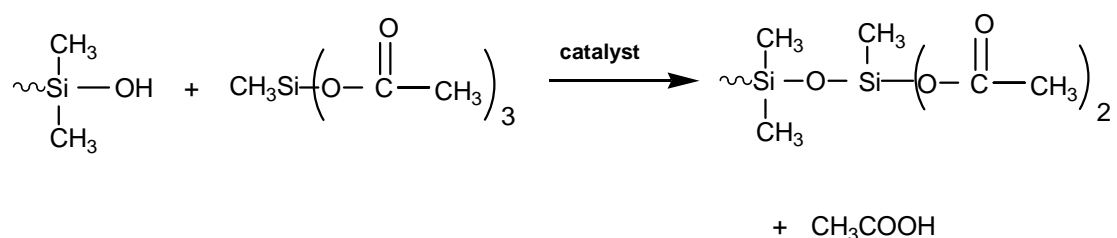
1. By end-capping the silanols with a moisture reactive crosslinking group to form a one-component sealant that cures in contact with atmospheric moisture at room temperature – these sealants are commonly referred to as RTV-1 (room temperature vulcanisable, one-component).
2. By making a two-component system, with one-component containing the silanol and the other containing the crosslinking agent (plus a catalyst). These systems are called RTV-2 (room temperature vulcanisable, two-component).

Most silicone sealants are based on RTV-1 systems. RTV-2 systems are rarely used as sealants, although in speciality applications they offer the benefits of fast curing and deep-section curing.

The hydrolysable end-capping groups in RTV are mostly trifunctional silanes.

RTV silicones are classified according to the by-product emitted during the curing reaction. The most common type are acetoxy sealants using methyl triacetoxy silane end-cappers and emitting acetic acid.

In the manufacturing process the organosilane reacts with the silanol end-groups in the presence of a condensation catalyst (shown here for an acetoxy sealant):



Examples of catalysts for this reaction are stannous octoate and dibutyltin dilaurate.

The curing reaction with atmospheric moisture links the end capped chains together to form a crosslinked elastomer and liberates the by-product:

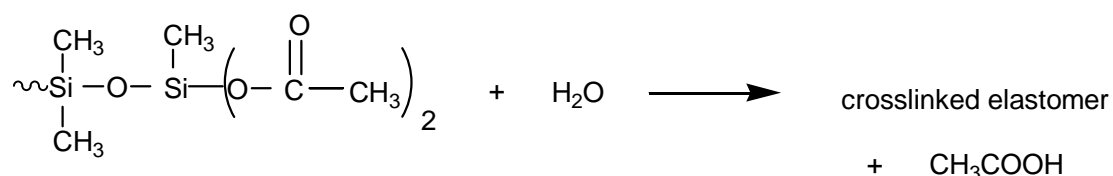


Table 4.16 shows acetoxy and the other most common silanes used and the chemical type, based on their by-products.

Table 4.16 Acetoxy and 'low odour' silicones		
Type of silicone	Typical silane	Odour of leaving group
Acetoxy	$\text{CH}_3\text{Si}\left(\text{O}-\text{CH}_3\right)_3$	'Vinegar' (acetic acid)
Alkoxy	$\text{CH}_3\text{Si}\left(\text{O}-\text{CH}_3\right)_3$	Low (methanol)
Methoxy		
Ethoxy	$\text{CH}_3\text{Si}\left(\text{O}-\text{CH}_2\text{CH}_3\right)_3$	Low (ethanol)
Oxime	$\text{CH}_3\text{Si}\left(\text{O}-\text{N}=\text{C}\begin{array}{l} \text{CH}_3 \\ \text{CH}_2\text{CH}_3 \end{array}\right)_3$	'Musty'
Amine	$\text{CH}_3\text{Si}\left(\text{O}-\text{NH}-\text{C}_6\text{H}_5\right)_3$	'Fishy'
Amide	$\text{CH}_3\text{Si}\left(\text{O}-\text{N}\begin{array}{c} \text{O} \\ \parallel \\ \text{C}-\text{C}_6\text{H}_5 \end{array}\right)_3$	'Mousy'
Ketoxy	$\text{CH}_3\text{Si}\left(\text{O}-\text{C}\begin{array}{c} \text{CH}_2 \\ \parallel \\ \text{C}-\text{CH}_3 \end{array}\right)_3$	'Fruity' (acetone)

Acetoxy sealants are characterised by their distinctive 'vinegar' odour and are used widely as construction and household sealants. They cure quickly and have good adhesion to many substrates. Their disadvantage is their unpleasant odour and the fact that the acetic acid can cause corrosion in many metal substrates. These negatives factors have encouraged the development of low odour sealants based on alternative silanes, although it is difficult to match the cure speed and adhesion of acetoxy sealants.

A special class of silicone sealants is called addition cured, whereby a hydride end-capped siloxane is added to a vinyl terminated siloxane, usually with a platinum based catalyst. Heat is usually required to get reasonable cure speeds. There is no-by product emitted during this reaction.

Table 4.17 shows the advantages and disadvantages of silicones.

Table 4.17 Advantages and disadvantages of silicone sealants	
Advantages	Disadvantages
Outstanding heat resistance Excellent low temperature properties Bond a wide range of materials Good moisture resistance Excellent UV resistance Inherently very flexible Biocompatible Excellent electrical properties 100% solids systems	Poor gasoline resistance Cannot be painted Acetoxy silicones corrosive to metals High moisture vapour transmittance Poor deep section curing Low tear strength Relatively expensive

A typical RTV-1 sealant comprises:

- Silanol-terminated polydimethyl siloxane
- Methoxy-terminated polydimethyl siloxane
- Moisture reactive crosslinker
- Catalyst
- Reinforcing filler
- Other fillers
- Adhesion promoters
- Other additives

Non-reactive methoxy-terminated polydimethyl siloxanes are used as plasticising extenders.

The use of reinforcing fillers is a key element of manufacturing RTVs. Unless reinforced, silicone polymers are soft ‘cheesy’ materials. High surface area fumed silica is the main reinforcing filler used. Both hydrophobic and hydrophilic fumed silicas can be used for specific applications.

Other fillers such as calcium carbonate, zinc oxide or quartz may be added to improve specific properties, modify flow properties or lower costs. In all cases, materials should be very dry to maximise shelf life of formulations.

Organosilane adhesion promoters are key ingredients of silicone sealants to improve adhesion to many surfaces and minimise loss of adhesion due to surface hydrolysis.

Other additives include pigments, heat stabilisers and fungicides.

Silicones are high performance sealants used in several industries.

Their major benefits include outstanding flexibility over a very wide temperature range with high temperature resistance to 260 °C, outstanding weatherability, biocompatibility and excellent electrical properties.

Weaknesses of RTV silicones include poor gasoline resistance that limits many automotive applications. Also, although silicones are the major specified high performance sealant in the construction industry, the fact that the cure is initiated by diffusion of moisture from the outside means that deep section curing is very difficult and cures greater than about 12-13 mm are not recommended. The inability to paint most silicones is also a limitation.

Low modulus RTV sealants are a leading sealant in the construction industry because of their outstanding ability to withstand weathering. The joint movement capability of silicones in construction joints can be up to 100% in expansion or 50% in compression.

Medium to high modulus silicones are used in structural glazing where the products act as both sealants and structural adhesives.

Silicones are also used as secondary seals in double glazing applications and as general purpose exterior weather-sealing of windows.

Medium modulus sealants are used in the automotive industry for sealing and gasketing and as general purpose sealants in marine applications.

A large volume of RTV sealants is used in general purpose caulking and sealing in bathrooms and kitchens at both the professional and DIY level.



The electronics industry uses silicones for potting and encapsulation because of their excellent electrical sealing capabilities.

The major RTV silicone producers are:

- Dow Corning
- General Electric/Bayer/Toshiba
- Wacker
- Shin Etsu
- Rhodia

Dow Corning is by far the largest supplier with around 40% of the market. GE, including its joint ventures with Bayer in Europe and with Toshiba in Japan is second with around 20%.

Other companies who are important formulators of silicones include Nusil, Permatest, Tremco (all US), Three Bond (Japan) and Makroflex (Finland).

North America is the largest market for silicones in terms of capacity, production and consumption of sealants. The two global leaders in silicone production, GE and Dow Corning are based in the region and other major suppliers have production and finishing facilities there.

Total annual consumption of RTV silicones in North America is estimated at 85,000 tons. There do not appear to be any planned capacity expansions in this region.

European demand for RTV silicones is estimated to be about 83,000 tons.

Further capacity is being installed or has recently been commissioned by both Dow Corning and Wacker.

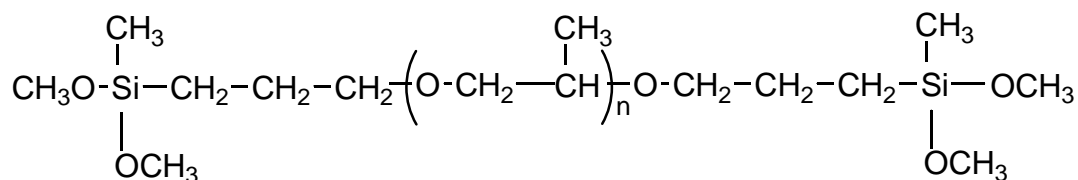
Far East consumption is 50,000 tons with Japanese consumption of silicones at 27,000 tons.

GE Silicones and Shin-Etsu Chemicals are to build a joint production plant in Thailand to manufacture silane monomers and siloxanes.

Shin-Etsu has independently expanded a silicone rubber plant in Selangor, Malaysia, and is building a new plant in China.

#### 4.12 Silyl Terminated Polyethers

The Japanese company Kanaka Corporation, have developed unique sealants that have polypropylene oxide backbones, just like in polyether polyol base polyurethanes, but end-capped with methyl dimethoxysilane groups:



**silyl terminated polyether**

These polymers can react with moisture, liberate methanol and crosslink just like one-component methoxy RTV silicones.

These sealants have been classified by the Japan Sealant Industry Association as modified silicone (MS) sealants. This is an unfortunate description because the term silicone should be used for polymers with exclusively a Si-O-Si backbone. The terms silane modified polyether or silyl terminated polyether are better descriptions.

They differ from polyurethanes in not containing urethane linkages from isocyanate groups and do not possess many of the unique properties associated with polydimethyl siloxanes. However, they do have very good properties and an excellent track record in the Japanese construction industry.

They are particularly useful for applications where their non-staining characteristics and excellent adhesion provide long-term use without significant changes in properties. They are also noted for their low viscosities at low temperatures, which aids in application.

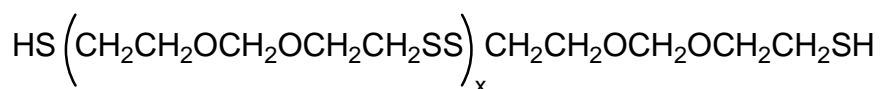
These sealants are low cost alternatives to silicones in many applications. They are not recommended for applications to glass surfaces and their limited high temperature resistance (90 °C) eliminates their use in many silicone type applications in industrial market segments.

These sealants are produced by Kanaka Corporation, with plants in Japan and Europe. In 2000, demand in Japan was around 40,000 tons, which is around 38% of all construction sealant volume. In Europe, demand in 2001 was around 10,000 tons or about 4% of the total market. There is very little usage of these sealants in North America where the leading silicone producers, Dow Corning and GE dominate the market.

#### 4.13 Polysulfides

Liquid polysulfides were discovered accidentally in 1926 by Dr. Joseph Patrick of Kansas City, US while in search of an inexpensive antifreeze. Instead of antifreeze he made a gummy mass that bounced and he called the material Thiokol, from the Greek words thio for sulfur and kol for rubber. This discovery led to the formation of Thiokol Corporation, later to become Morton Thiokol in the 1960s and to the development of liquid polysulfide polymer (LP<sup>®</sup>), sealants.

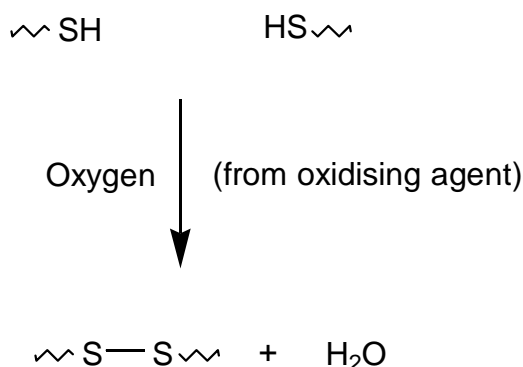
Polysulfides owe their unique properties as sealants to the presence of both sulfur atoms and formal groups (-CH<sub>2</sub>-O-) in the polymer backbone:



The formal groups contribute flexibility while the sulfur imparts excellent chemical resistance.

Other polysulfides have been based on the use of liquid thiol-terminated polymers based on polyether urethane backbones and polythioether backbones to yield sealants with enhanced strength and thermal stability.

The curing of polysulfides is a condensation reaction between the terminal thiol groups in the presence of an oxidising agent, which gives sulfur-sulfur linkages and liberates water. This reaction causes chain extension and crosslinking to give an elastomer.



Typical oxidising agents are lead dioxide, manganese dioxide, dichromates and peroxides, although lead dioxide has been phased out because of its toxicity.

Polysulfides are used as construction sealants, marine sealants, industrial sealants and in aerospace applications, particularly as jet fuel tank sealants. They are also used in the insulated glass market by window manufacturers to bind together for double glazing applications, but have lost most of their market share to butyls in recent years.

In addition to their use as sealants, polysulfides are also used as flexible hardeners for epoxy resins.

Rohm and Haas acquired the successor to Morton Thiokol, Morton Chemicals, but ceased production of polysulfides at the end of 2001. Thiokol™ Liquid Polysulfides are still available from Toray Fine Chemicals (Japan) and Polyspec (US). This action by Rohm and Haas removed some 30% of the worldwide capacity.

The leading European formulators of polysulfides are Chemetall, Colfirmit Rajasil, Fenzi, Henkel Teroson and Kömmerling

The global market for polysulfide sealants is around 37,000 tons valued at \$120 million but the construction uses are under attack from alternative sealants such as high performance silicones and polyurethanes.

#### 4.14 Plastisols

Vinyl plastisols are dispersions of special, fine particle size PVC resins in plasticising liquids. Plasticisers are typically phthalates, isobutyrate and benzoates. Plastisols are liquid at room temperature. However, when heated to 140-200 °C, fusion takes place and the liquid is converted into a tough, elastomeric solid.

Due to their low cost and pseudoplasticity (shear thinning nature), plastisols are particularly suited for application by means of airless spray systems for automotive underbody protective coatings to give rust and gravel protection. Special versions use additives such as trifunctional methacrylates to give better durability.

Automotive plastisol sealants are also used in sealing body cracks and seams at the body-in-white stage of car manufacture and cured in the paint-bake ovens. Thirteen to eighteen kilos of sealant are used per car.

Plastisols are also used to seal automotive oil and air filters.

#### 4.15 Other Sealants

Asphalts and coal tar resins are low cost materials produced in oil refining and in the distillation of coal tar, respectively. They are used extensively as hot-applied highway and airfield joint sealants.

Improved properties are obtained by blending with other resins and rubbers, for example, rubber-asphalt, coal tar-PVC, and coal tar-urethane.

Naturally occurring asphaltic materials called Gilsonites are used in the auto industry as body seam sealers, but are being supplanted by plastisols.

Low cost and low performance sealing caulks based on filled drying oils are still marketed in the DIY and factory glazing markets.

The sealing of threaded joints and gaskets in liquid oxygen systems cannot be accomplished with organic sealants because of the danger of combustion. Polytetrafluoroethylene (PTFE) tape is used for this purpose, and special sealants based on gelled fluorocarbon oils and fluoroelastomers, often filled with PTFE, have also been developed.

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## **5 Additives for Adhesives and Sealants**

Most adhesive and sealant families are defined by the basic monomers or polymers used in the formulations. However, additives are key ingredients in most systems. Additives for adhesives and sealants can be defined as materials added in small or large amounts to adhesives and sealants either physically dispersed in or dissolved without affecting significantly the basic molecular structure. Additives do, however, often have a significant effect on the curing, performance and final properties of the products.

Additives are generally classified according to their specific functions rather than their chemical basis.

Additives include:

- Catalysts (or initiators)
- Stabilisers
- Colourants
- Fillers
- Plasticisers
- Rheology control additives
- Tougheners
- Adhesion promoters
- Tackifiers

From a marketer's perspective additives can be defined as derived demand products.

This means that the market demand for additives is not inherent but rather results from the supply and demand patterns of the adhesives or sealants for which they are used. These polymers in turn are part of a derived demand channel leading to final consumables such as automobiles, consumer durables, disposables and so on. However, in contrast to the rubber chemicals industry where a small number of very large end-users (the tyre industry) has created tremendous price pressures on a small number of suppliers, the adhesives industry is still highly fragmented and many additives are used in small quantities and are very profitable items for suppliers.

Being towards the upstream end of the supply chain means that additives are subject to a very wide range of influences. These range from direct developments in the adhesives industry to macroeconomic effects.

Some additives are added by raw material suppliers, e.g., stabilisers in monomers, but most are added by the adhesive manufacturers.

### **5.1 Catalysts**

Catalysts, or initiators, are used widely in several adhesive systems for polymerisation or crosslinking. They can be present as key ingredients in one-component systems, such as in anaerobics or UV adhesives, or be used as a second component, such as in epoxy adhesives or reactive acrylics.

Examples of catalysts include peroxides, hydroperoxides, peresters, photoinitiators, tertiary amines and transition metal salts for acrylic systems; amines, anhydrides and mercaptans for epoxies, and photoinitiators for UV adhesives.

## **5.2 Stabilisers**

Stabilisers in adhesives and sealants are used in general to increase shelf life of the products by preventing premature polymerisation or to improve properties such as heat resistance. Examples include quinone derivatives and metal chelators like EDTA for free-radical systems, moisture scavengers for polyurethanes and cationic epoxies, strong acid stabilisers for anionic systems such as cyanoacrylate adhesives, and ferric oxide pigments for heat stability in silicones.

## **5.3 Colourants**

Colourants include organic dyes, pigments such as  $\text{TiO}_2$ , fluorescent pigments and pearlescent pigments – coated particles of mica with  $\text{TiO}_2$ . Fluorescent additives are also added to some adhesives to detect the presence of adhesive on parts.

## **5.4 Fillers**

A wide range of fillers are used in adhesives and sealants, both as extending materials and to modify properties. They include:

- Calcium carbonate
- Mica
- Slate flour
- Zircon
- Alumina
- Glass microspheres
- Barytes
- Talc
- Marble flour
- Silica
- Vermiculite
- Aluminium
- Precious metals
- Phenolic microspheres
- Kaolins

In some cases, a filler is a key ingredient in a system. For example, fumed silica is added to RTV silicones as a reinforcing filler.

## **5.5 Plasticisers**

Plasticisers are substances added to an adhesive or sealant to increase its flexibility, workability, or dispensability.

Plasticisers are classified as either non-reactive or reactive types.

Examples of non-reactive plasticisers are:

- Benzoates
- Sulfonamides
- Phosphates
- Isobutyric acid esters
- Phenols
- Adipates
- Citrates
- Oleates
- Ricinoleic acid esters
- Hydrocarbon oils
- Phthalates
- Polyesters
- Sucrose esters
- Chloroparaffins
- Abietic acid esters
- Azelates
- Sebacates
- Stearates
- Glycolates



Examples of the use of plasticisers include:

- (1) **Latex Adhesives** – Much latex adhesive is based on homopolymer polyvinyl acetate emulsion or ethylene-vinyl acetate copolymer. Benzoates are the predominant plasticisers for this area and are used to increase flexibility.
- (2) **Latex Sealants** – Most sealants utilise acrylics or vinyl acrylic polymers as the base. Plasticisers are utilised in most sealant formulations to achieve a good balance of performance characteristics at reasonable costs. Benzoates and phthalates are the main plasticisers used.
- (3) **Polyurethane Sealants** – Plasticisers are used in one and two part polyurethanes basically to soften and make the system more workable. Benzoates, phthalates and chlorinated paraffin types are used.
- (4) **Polysulfide Sealants** – In two part polysulfide sealants, plasticisers can be utilised in both sides of the formulation. On one side, the polymer side, the plasticiser is used to soften and on the catalyst side, the plasticiser can be used as the dispersion media. Benzoates and phthalates are commonly used.
- (5) **Hot Melt Adhesives** – Most hot melt adhesives produced do not require the use of plasticisers. However, in high vinyl acetate EVA copolymers or SBR copolymers, solid and liquid plasticisers may be used to soften and modify application characteristics of the hot melt system. In particular, 1,4-cyclohexane dimethanol dibenzoate has found use in block copolymer and ethylene-vinyl acetate glue sticks.
- (6) **Vinyl Plastics** – Plasticisers are key ingredient in these compounds and serve to liquefy the compositions and flexibilise the PVC after fusion by heat. Phthalates, isobutyrate, benzoates and oily secondary plasticisers are the common materials used.

In some systems, reactive plasticisers are used. For example, in epoxy adhesives, the inherent brittleness of these adhesives can be lowered by using monofunctional epoxy additives, which function by lowering the crosslink density of the systems. Similarly, in anaerobic adhesives, monofunctional methacrylate monomers or oligomers can be used.

## **5.6 Rheology Control Additives**

Additives can be added to adhesives and sealants to increase their viscosity or control their rheology. The most common rheology desired in adhesives and sealants is pseudoplastic (shear thinning) or thixotropic (time-dependent shear thinning). Fillers or dissolved polymers often serve to give a thick pseudoplastic system whereas hydrophilic or hydrophobic fumed silicas are the most common ingredients used to increase thixotropy.

## **5.7 Tougheners**

Some adhesive systems are inherently brittle, including epoxies, cyanoacrylates and highly crosslinked acrylics. To flexibilise and increase the impact resistance of these systems, rubbers are often incorporated. Examples are ethylene acrylic rubbers in cyanoacrylates and styrene block copolymers in reactive acrylics. Frequently the rubber has functionality to copolymerise in with the base adhesive. Examples are carboxy terminated or vinyl terminated nitrile rubber in epoxies and chlorosulfonated polyethylene in reactive acrylics.

## **5.8 Adhesion Promoters**

Adhesion promoters are key additives in several technologies. In some cases, they are specific to a particular system, for example, the use of acrylic or methacrylic acid as comonomers in anaerobics or reactive acrylics gives enhanced adhesion to metal surfaces.

Organosilane additives have proved to be very versatile adhesion promoters for several systems, including silicones, reactive acrylics and epoxies. These molecules contain hydrophilic and hydrophobic moieties and act as a coupling system between the organic adhesive or sealant and metal or glass surfaces. In addition to enhancing adhesion, they provide resistance to hydrolytic degradation of adhesive bonds.

## **5.9 Tackifiers**

Tackifiers are added, particularly to pressure sensitive adhesives and hot melts, to increase the instant grab known as tack. Most tackifiers are based on petroleum or natural resins. Examples are:

- Wood rosins
- Gum rosins
- Tall oil rosins
- Aliphatic C<sub>5</sub> resins
- Aromatic C<sub>9</sub> resins
- Cycloaliphatic resins

## **5.10 Fungicides**

Fungicides are added to latex and other water-based systems to control fungus and bacteria, both during the manufacturing operation and in storage.

## **5.11 Additive Suppliers**

Many companies supply additives to the industry.

Examples include:

Photoinitiators – Ciba Specialty Chemicals, Sartomer

Pigments – Ferro, Day-Glo

Plasticisers – Bayer, BASF, C.P. Hall

Fungicides – Dow Chemical, Lonza, Rohm and Haas

Peroxides – GEO® Specialty Chemicals, Akzo Nobel

Fumed silica – Cabot Corp., Degussa

Tackifying resins – Hercules, Eastman Chemicals, Arizona Chemicals, Exxon Mobil

Silanes – Dow Corning, Petrarch, Crompton, Wacker

Tougheners – Novachem, DuPont Dow Elastomers, Kraton

## **6 Classification and Comparison of Adhesives and Sealants**

### **6.1 Commodity, General Purpose and Speciality Adhesives**

There are various ways of classifying adhesives and sealants, e.g.:

- As natural or synthetic substances
- By chemistry, e.g., acrylic, epoxy
- As thermosets or thermoplastics
- As one-component or two-component systems
- As commodity or speciality products
- As structural or semi-structural or non-structural
- By cure mechanism, e.g., anaerobic or UV cured
- By market segment served

The way one chooses to classify them depends on whether you are a chemist, marketer, salesman, market researcher or analyst.

Ultimately, the customer doesn't care about the technology or cure mechanism. He is looking for a cost-effective solution to his bonding problem.

I believe that market forces have caused adhesives to evolve into three general categories:

- Commodity adhesives
- General purpose adhesives
- Speciality adhesives

Commodity adhesives are those whose raw materials fluctuate according to supply and demand, where supply exceeds demand or where there has been a concentration in the customer base. Commodity adhesives:

Formaldehyde resins, PF, UF and MF  
Starch and dextrin adhesives  
SBR latex for carpet manufacture

General purpose adhesives are those where large volumes are sold but where there are still opportunities for product differentiation. General purpose adhesives:

Latex adhesives  
Hot melts  
Pressure sensitive adhesives  
Solvent based adhesives  
Inorganic adhesives

Speciality adhesives are often custom formulated for specific applications or sold in such low volumes that they demand high prices. Speciality adhesives:

Polyurethane  
RHMU  
Epoxies  
Cyanoacrylates  
Anaerobics  
Reactive acrylics  
UV adhesives

A specific adhesive is chosen for a particular application because it has the requisite performance, productivity and cost, compared to alternative adhesives or other methods of fastening.

It is very useful to look at the materials being bonded and compare the relative merits of different adhesives and sealants plus compare them to alternative methods of fastening, both from a performance and productivity point of view.

## **6.2 Bonding of Metals**

Although new materials like plastics and composites have replaced metals in many industrial and household products, metals will continue to be used where their unique combination of properties such as high strength and high temperature resistance are coupled with low cost.

### **6.2.1 Adhesive Bonding Versus Alternative Techniques**

Adhesive bonding is usually not the only possible joining method available to the design engineer.

Table 6.1 shows the strengths and weaknesses of adhesive bonding of metals compared to other methods.

<b>Table 6.1 Comparison of assembly methods for metals</b>						
	<b>Adhesive bonding</b>	<b>Mechanical fastening</b>	<b>Soldering/brazing</b>	<b>Arc Welding</b>	<b>Spot welding</b>	<b>Riveting</b>
<b>Joint stresses</b>	Uniform distribution	Point of high stress at fasteners	Fairly uniform distribution	Fairly uniform distribution	Local stress points in structure	Local stress points in structure
<b>Fatigue resistance</b>	Excellent	Need to prevent vibration loosening	Good	Special methods often necessary to enhance resistance	Often poor	Good
<b>Use for dissimilar metals ?</b>	Excellent for most combinations	Usually good - some problems with soft metals	Some capability	Limited capability	Limited capability	Excellent
<b>Joint preparation</b>	Cleaning and pre-treatment often necessary	Hole drilling or tapping required	Pre-fluxing necessary	Little or none required	Little or none required	Holes when non-piercing rivets used
<b>Temperature resistance</b>	Limited	Very high	Limited by softening point of metals used	Very high	Very high	Very high
<b>Joint appearance</b>	Invisible bondlines	Surface discontinuities often show	Usually acceptable	Usually acceptable	Surface discontinuities often show	Surface discontinuities often show
<b>Production speeds</b>	Slow to fast depending on adhesive type	Slow to medium	Can be very fast	Can be very fast	Can be very fast	Can be very fast
<b>Material costs</b>	Low	High	Medium	Low	Low	High
<b>Operating costs</b>	Low	Medium	Medium	High	Medium	Medium
<b>Capital costs</b>	Low	Low	Low	High	High	Low

Other technologies and combinations of technologies that are being used quite widely are:

- Mechanical clinching – this is a form of mechanical fastening which involves the joining of two sheets of metal by deep drawing the sheets into a cup shape using punch and die tooling.

- Clinch bonding – This technique combines mechanical clinching and adhesive bonding.
- Weld bonding – This is a process that combines adhesive bonding with resistance spot welding and is carried out by either spot welding through an uncured adhesive joint or by flowing adhesive into a spot welded joint. The spot welding is often used to fixture the assembly while the adhesive cures.
- Rivet bonding – the combination of a small number of rivets and a structural adhesive can usually give a much stronger assembly than a large number of rivets used alone. This process has been widely used in the assembly of school buses for many years.

### **6.2.2 Bonding of Lightweight Metals**

In addition to the joining of iron and steel, technologies for the joining of other metals are being researched in order to produce assemblies of exceptional strength and durability under high stress situations and in hostile environments. One driving force for using alternative metals is the tremendous weight savings that can be achieved through the use of so-called ‘light metals’ such as aluminium and magnesium. This is of particular interest to the automotive industry where weight savings can be translated into considerable gains in both fuel economy and performance.

Aluminium is 60% lighter than steel and has a very good strength to weight ratio. The metal has excellent corrosion resistance and is used widely in industrial, construction and consumer goods. A wide variety of aluminium components (mainly castings) is used in the automotive industry. The amount of aluminium in US cars and light trucks increased from 83 kilos in 1991 to 113 kilos in 1999.

The use of aluminium sheet offers considerable potential to reduce the weight of an automobile body. In current construction, the vehicle consists of stamped steel body panels, spot welded together (described as ‘body-in-white’) to which stamped steel fenders, doors, hood, and deck lid are bolted.

An aluminium body structure may be fabricated either as a stamped alternative to a steel structure or as a ‘spaceframe’ system, which consists of castings, extrusions and stampings joined together.

Spot welding of aluminium sheet requires special welding equipment and significantly more electrical power compared to spot welding steel. Furthermore, the spot welding process changes the microstructure of the base material in the area surrounding the weld. This change in microstructure can significantly reduce the fatigue strength of the joint.

Magnesium is the lightest metal that is stable under normal ambient conditions and produced in quantity. It is 33% lighter than aluminium and 75% lighter than steel and iron. Magnesium and its alloys have several advantages over ferrous materials and aluminium, including higher elongation, outstanding machinability and easier casting. Magnesium alloys do have some property disadvantages that limit their utility in many applications. Magnesium has 25% less ultimate tensile strength than aluminium, 35% lower fatigue strength, 40% lower modulus and hardness is 25% lower. However these weaknesses can often be overcome by good component design. Magnesium ingots cost about 50 to 100% more per unit weight than aluminium; however, it is the cost per unit volume that is often important in the manufacture of components. Since magnesium is one-third less dense than aluminium, its cost per unit volume can be nearly the same or even lower when the aforementioned ease of manufacturing is taken into account. Magnesium is widely used in the manufacture of many lightweight industrial and household goods.

Adhesives have been used for several decades for the structural bonding of iron and steel. Other non-ferrous metals like aluminium, magnesium and titanium have been bonded in the construction of aircraft, often in combination with other fastening methods such as rivets. Lengthy and

expensive pretreatment and curing processes have been designed to ensure absolute reliability in bonded joints, both in terms of structural strength and resistance to corrosion. Although this experience gives confidence to the non-aerospace design engineer, most of the assembly processes used in aerospace are totally incompatible with the rapid production line assembly operations practiced by industrial and automotive manufacturers.

### **6.2.3 Recent Developments in Aluminium Bonding**

Historically, with the exception of aerospace applications, most in-depth adhesive studies have been involved with ferrous substrates like steel and cast iron. Because of the interest in using lighter weight metals, particularly in the auto industry, there has been considerable activity in the bonding of aluminium. This work is important because much of the data will be able to be extrapolated for the bonding of aluminium to other metals as long as the important differences, such as possible galvanic corrosion, and the differences in thermal expansion coefficients are recognised.

Alcoa researchers [1] compared different methods of joining aluminium to determine its suitability for automobile body construction. Because the automobile body is designed for stiffness, most structural parts sustain relatively light loads. However, certain points in the structure, such as attachment points for suspension components and engine mounts, are very highly loaded. In these cases, fatigue is a major consideration. The authors point out that since the curb weight of an aluminium intensive vehicle is 25% less than for a steel automobile, stresses in the aluminium body are correspondingly lower. Fatigue and static strength testing of joints with various aluminium alloys show that adhesive bonding, rivets, rivet bonding and weld bonding all outperform spot welds and have greater performance than that required for the application. In crush-test specimens, adhesive bonding alone gave some indication of failure due to peel forces. Warren [2] at Alcan described the assembly of aluminium automobile panels using weld bonding with a rubber toughened epoxy adhesive.

In work sponsored by the aluminium industry and by Audi and BMW, Lachman [3] compared the bonding of steel and aluminium alloys using three epoxy adhesives. Steel was used in a bare state and also zinc coated. Bonds were tested immediately after curing and after several months weathering. It is concluded that with both metals, adhesive bonding gives much better fatigue life than spot welding. All weathered specimens show some reduction in fatigue life, although corrosion is the dominating degradation mechanism in the steel specimens and diffusion of moisture to the adhesive-metal surface in the case of the aluminium alloys.

Authors from 3M [4] described the testing of two speciality epoxy adhesives for aluminium, designed for hem flange bonding and panel bonding respectively. These adhesives show outstanding sustained load durability in cyclic corrosion tests even when stressed to 40% of their initial shear strengths.

Ford Research Laboratories [5] have evaluated the fatigue behavior of aluminium alloy joints and show the enormous benefit of using an epoxy adhesive in combination with spot welding or mechanical clinching. Weld bonding improves fatigue strength approximately 400% over spot welding and clinch bonding approximately 325% over clinching alone. The authors attribute the improvements to the increase in overall bond area when adhesives are used, the stiffness provided to the joint area by the adhesive and to the fatigue resistance of the adhesive itself.

Work in the UK [6] described the attachment of stiffeners to steel and aluminium alloy plates using epoxy and reactive acrylic adhesives. The results of fatigue testing suggested significant improvement over welded specimens. A significant finding was that the high modulus epoxy adhesive failed by cracking in the adhesive layer, whereas the lower modulus tough acrylic adhesive showed no cracking and final failure was always in the metal plates.

As part of a US Army sponsored program, Martin Marietta Laboratories [7] conducted mathematical joint analysis and tested prototypes of tubular aluminium alloy joints bonded with a toughened adhesive. It is found that the tubes fail by tubular buckling at loads considerably lower than the expected limit load of the bonded joint.

Davies and co-workers [8] describe the improvement in adhesive bonding of aluminium alloys by anodizing prior to bonding. The work shows that the morphology of the oxide and penetration of the adhesive into the porous oxide strongly influences bond performance.

#### **6.2.4 Bonding of Dissimilar Metals**

Alcoa researchers [9] investigated the bonding of three mill finish aluminium alloys to steel for potential use in automobile body panels. The alloys were a heat-treatable aluminium-copper alloy, a non heat-treatable aluminium-magnesium alloy and a heat-treatable aluminium-magnesium-silicon alloy. In this study, lap shear and peel specimens were prepared and treated under processing conditions currently used for steel designs. Aluminium substrates were prepared by vapour degreasing and alkali cleaning. The steel substrates were cleaned by wiping with methyl ethyl ketone (MEK) solvent. Following the cleaning steps, a water-based forming lubricant was applied to the aluminium and the same lubricant or an anti-corrosion oil was applied to the steel. Stiffeners were attached to the specimens to eliminate bowing caused by the difference in thermal expansion coefficients between the two metals. Following assembly with adhesive and curing, the assembled panels were zinc phosphated and electrocoated (E-Coat), which are established procedures for steel surfaces to provide corrosion resistance and improve paint adhesion respectively.

Adhesives studied were a wide range (30 adhesives) of epoxy, toughened epoxy, epoxy urethane and tough acrylics. Joint strengths of specimens were measured at room temperature and at 100 °C, after immersion in common salt solutions and after exposing to 100% relative humidity conditions for periods up to 60 days. Long-term outdoor exposure was also carried out. Many adhesives gave lap shear strengths of over 14 MPa (2000 p.s.i.) when tested at room temperature and peel values of 70-175 N/cm (40 to 100 p.l.i.) However, testing at 100 °C began to show dramatic differences between adhesives. At this temperature we expect to see both the effects of softening of the adhesive itself and the results of internal stresses set up by the differences in thermal expansion coefficients of the metals. All of the adhesives showed significant decreases in shear strength with only four retaining strengths greater than 10.5 MPa (1500 p.s.i.). Humidity was by far harshest environment for the specimens. Many of the adhesives did not survive the duration of the test and peel strength decreased significantly in both the humidity and immersion testing. Only two adhesives, a toughened epoxy and an epoxy-urethane retained strength with all three alloys and under all environmental conditions. These adhesives were chosen for long-term outdoor testing for periods up to 6 years.

A significant finding from this work is that there is no evidence of galvanic corrosion in the specimens, either in the accelerated testing or in the long-term exposures after one year. It is encouraging that bonds involving aluminium substrates appear to be less susceptible to environmental damage than those with steel, because this is a factor that has limited the use of structural adhesives on steel. Indeed, Pocius and co-workers [10] showed that in comparing the bond durability of steel and aluminium, dry lap-shear strengths can be similar, but stressed lap-shear joints of steel substrates that are exposed to a humid environment fail in less than 30 days while the aluminium joints last for more than 3,000 days.

Japanese researchers [11] described a stress analysis of butt joints of steel to aluminium where joints were assembled with epoxy adhesives and were subjected to cleavage loads. They found that the normal and shear stresses are maximised at the edge of the interface on the load application side between the adherands and the adhesive bond. However, both stresses are greater at the edge of the interface between the higher modulus adherand (steel) and the bond.

Ikegami and co-workers [12] studied the connecting of two shafts using a bonded cylindrical coupling instead of flanges. The shafts were steel and the couplings either aluminium alloy or brass. On bonding with an epoxy adhesive, good correlation was found between calculated joint strengths and the initial failure load of the joint.

Aluminium bicycle frames are being successfully bonded with epoxy adhesives to replace traditional brazing methods. A process developed by the Raleigh Cycle Company and Permabond International utilised a Permabond ESP epoxy adhesive to bond aluminium alloy frame tubes to steel lugs and stays. After heat curing, these frames withstood a minimum 55 MPa (8000 p.s.i.) tensile strength test. Usually the metal tube collapsed before the bond broke.

### **6.2.5 Adhesive Technologies for the Bonding of Dissimilar Metals**

The number of adhesive technologies for load bearing applications is somewhat limited. Most thermoplastic systems, for example hot melts, are totally excluded because they will creep under load, particularly at elevated temperatures. Highly crosslinked structures are necessary to support loads.

Epoxy adhesives have been the major adhesive family used for structural bonding in the aerospace, industrial and automotive industries. They are characterised by curing to hard infusible resins that bond to a wide range of surfaces and have excellent heat and environmental resistance (see Section 4.2). Both two-component and heat cured versions are available and literally thousands of formulations have been developed over the years for specific applications. One of the traditional weaknesses of epoxies, namely, their brittleness, has been the focus of research attention for the last 20 years or so. Significant breakthroughs have been made to produce tough and more flexible epoxies by the incorporation of rubbers such as carboxy terminated butadiene-acrylonitrile (CTBN). The necessity for long cycle times for heat curing has been mitigated in many automotive and industrial applications, firstly by using current paint bake ovens in the automotive industry to cure the adhesives and secondly by using technologies like induction heating where parts can be fixtured in seconds. Most industrial epoxies are priced in the \$6 to \$13 per kg range, making them very cost effective for many applications. Speciality products can sell for \$22 to \$50 per kg.

Reactive acrylic adhesives are two-component 100% reactive systems, based on methacrylate and acrylate monomers which are toughened with dissolved rubbers and are cured either by using a surface primer, or by mixing two-components together (See Section 4.1.3). These adhesives have proved to be extremely useful in demanding metal bonding applications where fixture times of a few minutes and strong, impact resistant bonds are required. They often compete very effectively with epoxy adhesives.

An attractive feature of acrylic adhesives is that, with very few exceptions, they are formulated from commercially available monomers that are available at relatively low costs. These adhesives can be manufactured for \$6 to \$12/kg giving end user prices of \$17 to \$45/kg, which are reasonable for many general purpose industrial and automotive applications. Acrylic adhesives do have the inconvenience of being two-part systems and some have unpleasant odours and are flammable. However, the vast range of available raw materials makes them very attractive to the adhesives formulator. Also single component heat cured versions of these adhesives can be readily formulated.

## **6.3 Bonding of Plastics**

There has been a tremendous increase in recent years in the use of plastics to replace metals in component design. Since plastics do not always lend themselves to traditional methods of fastening, there have been increasing demands for adhesive bonding of these materials. Industries, like the auto industry, were slow initially to accept plastics but are now introducing them at a



frantic pace, particularly as plastics manufacturers are almost daily producing stronger and more easily processable materials. For example, almost all auto bumper systems are now made of plastic.

### 6.3.1 Problems Unique to Plastics

From the adhesives technologist's point of view, plastics are somewhat of an anomaly: on the one hand bonded joints can be made where the plastic fails before the adhesive; on the other hand certain plastics are very difficult to bond (Table 6.2).

All plastics can be joined successfully with the correct choice of adhesive, joint design and surface preparation.

<b>Table 6.2 Problems in bonding plastics</b>
Inherent flexibility of plastics
High thermal expansion coefficients
Stress cracking from liquids
Presence of mould-release agents
Low polarity surfaces

One of the significant differences between plastics and metals is the inherent flexibility of plastics. An unreinforced plastic is typically of the order of 100 times more flexible than steel. This flexibility means that joints designed to withstand shear forces will experience cleavage or peel forces as the plastic deforms under load. These forces lead to high concentrations of stress near the ends of the overlap, often leading to joint failure at low loads. The effects of the plastic flexibility can be minimised and controlled by choosing a higher modulus plastic (e.g., a reinforced material), shortening the bond overlap, increasing the thickness of the bondline, or by using a much more flexible adhesive.

Another major difference between metals and plastics is their thermal expansion coefficients. Whereas different metals do not vary widely in thermal properties - steel and aluminum vary by about a factor of two, plastics have much higher expansion coefficients and can vary quite substantially from plastic to plastic. Assemblies bonded using substrates with widely differing thermal expansion coefficients will suffer severe joint stresses and often fail under thermal cycling or thermal shock conditions. Choosing a more flexible adhesive and increasing the thickness of the bondline can partially compensate for these differences, but wherever possible a closer thermal match should be designed in. For example, filler loadings in plastics can change their thermal expansion coefficients substantially – the expansion coefficient of high density polyethylene is approximately halved by a 30% glass fibre loading.

An essential component for successful bonding of materials is good wetting and spreading of the adhesive on the substrate surfaces. To achieve this with conventional materials like metals or glass it is usually only necessary to ensure a good clean surface using appropriate and well established cleaning or etching procedures. However, with plastics the situation can be very different. In addition to common surface contaminants like dust and grease, many processing operations like injection-moulding use mould release agents to minimise adhesion of the plastic to the mould surface and aid removal of the component from the mould. These materials, which are typically silicones, fluorocarbons or metal stearates often cause serious problems.

One problem that is fairly unique to plastics is the danger of chemically damaging the plastic if an incompatible surface cleaner or adhesive is used. The extreme case of this is actual dissolving of the plastic with subsequent deformation of the part. A more common observation is stress cracking where incompatible liquids induce cracks, particularly in highly stressed plastics. This frequently occurs when the liquid adhesive is left in contact with the plastic for a long time. For example, the use of anaerobic threadlockers with crack-susceptible plastics where the combination of a highly

stressed threaded assembly coupled with uncured liquid adhesive outside the joint can often cause problems.

Plastics can be bonded either by using just simple solvents or with highly sophisticated adhesives. The oldest technique is to use a so-called solvent cement to create surface dissolving and ‘welding’ of the plastic. Although very useful for some plastics and still used quite frequently for plastics like flexible PVC, the method is rapidly being superceded by adhesives and is being legislated out with the intense government and public focus on toxic and flammable solvents. Table 6.3 lists the advantages and disadvantages of this technique.

<b>Table 6.3 Advantages and disadvantages of solvent ‘welding’ or cementing of plastics</b>	
<b>Advantages</b>	<b>Disadvantages</b>
Low cost Fast fixture times Strong bonds One-component	Poor gap-filling For thermoplastics only Difficult for dissimilar materials Possible stress cracking Flammability or toxicity of solvents

When we look at using adhesives to join plastics, there is a wide range of adhesive types available – epoxies, urethanes, solvent cements, cyanoacrylates, hot melts, silicones, etc. Choosing amongst these alternatives is not simple but by looking at several selection criteria and using a few guidelines, the choice can quickly be reduced to a few candidates. The most important thing to do when trying to select an adhesive is to totally evaluate the entire component design and assembly process and to try whenever possible to use both engineers and adhesive chemists together early in the design process.

Although the adhesives chemist is always working to make adhesives more versatile, no adhesive can totally compensate for a poor design or bad choice of plastic. A check-list of design and process criteria is a useful starting point.

- Substrate composition
- In service loads and environment
- Joint design
- Process factors
- Material cost constraints
- Capital cost constraints
- Productivity requirements
- Safety and environmental issues

Often compromises have to be made; for example one may use a very expensive fast-curing adhesive but make tremendous gains in productivity. In other cases a less expensive adhesive may be acceptable but necessitate long cure times in ovens.

### **6.3.2 Types of Adhesives for Plastics**

Modern adhesives for plastics typically are epoxies, cyanoacrylates, polyurethanes or reactive acrylics, although hot melts can often give good bonds. Solvent cements are still used but mainly in the plumbing industry.

- Epoxy resins are one- or two-component adhesives that adhere well to several types of plastics and maintain structural loads under severe environmental conditions. They excel in bonding composites for high temperature service. One-component systems are cured by heating at 70-130 °C for a few hours but this heat can be a problem for many thermoplastics. Two-

component systems cure in minutes to hours using amine or mercaptan hardeners. The major factor that has limited the penetration of epoxies into plastics bonding applications has been brittleness. Rubber toughened systems have improved this problem to a certain extent.

- Polyurethane adhesives for plastics are available primarily in two-component form. They are cured at room temperature or at elevated temperatures by reaction between an isocyanate component and a active hydrogen-containing material such as a polyester or polyether polyol. They are extremely versatile in plastics bonding and are used widely for polyester sheet moulding compound (SMC) bonding where their good adhesion and high flexibility are key properties. Limitations include the moisture-sensitivity of the isocyanates leading to foam formation, the need for primers for some surfaces, and some health and safety concerns regarding the toxicity and irritancy of isocyanates.
- Cyanoacrylates are probably the most versatile adhesives for plastics. They are rapid-curing single component adhesives which spontaneously cure at room-temperature when held between two substrate surfaces. They cure by a catalytic mechanism initiated by trace amounts of basic materials or even films of atmospheric moisture on the surfaces. Excellent adhesion to many plastics can be achieved. Limitations include gap filling only to 0.5 mm, temperature resistance to about 100 °C and poor impact resistance. Recent formulations have made considerable progress in mitigating these deficiencies for many applications.
- Reactive acrylics are based on methacrylate and acrylate monomers toughened with several types of rubbers. The adhesive is applied to one substrate and a primer to the other substrate. Fixture takes only 1 to 4 minutes after assembly at room temperature. Some versions of these adhesives use very volatile and high odour monomers, but much less hazardous systems have been developed. Reactive acrylics have excellent plastics bonding abilities due in part to their solvency for many plastics. However, this can cause stress cracking in some cases. The major limitation of this class of adhesive is limited gap-filling to about 1 mm. Two-part mixable versions of these adhesives have greater gap filling ability, leading to even greater capabilities for structural bonding and repair of plastics and composites.
- UV acrylics are also available which can be cured in 1-30 seconds using UV or visible light. These are used successfully on transparent substrates like PVC and polycarbonate.
- Silicones have traditionally been used as sealants rather than adhesives, but surprisingly good bonds can be achieved to many plastics. Single component silicones (RTVs) cure slowly at room temperature to give highly flexible systems. These systems often emit volatile cure by-products such as acetic acid or amines, which can be objectionable. Two-component systems can be formulated with no cure by-products and which cure very quickly. We expect to see significant advances in this area in the future particularly in view of the outstanding durability and flexibility of silicones over a wide range of temperatures.
- Hot melts are very versatile adhesives for plastics. Adhesives based on EVA, polyamides or polyesters give good adhesion to a wide range of plastics, although distortion can be a problem with some heat-sensitive materials. Limitations include limited heat resistance. Reactive hot melt urethanes have better heat resistance and are gaining market share in applications such as panel bonding.

### **6.3.3 Bonding of Some Specific Plastics**

Although the enormous range of plastics grades makes it impossible to recommend any specific adhesive, certain guidelines are appropriate for several classes of plastics.

Plastics can often be successfully bonded ‘as-received’ but it is good engineering practice to ensure that surfaces are clean before assembly. Solvent wiping with chlorinated solvents or alcohols can

remove dirt or mould release agents and light abrasion will often improve performance. Testing each treatment is always recommended prior to production use.

Glass fibre reinforced unsaturated polyesters are often referred to as ‘Sheet Moulding Compounds’ (SMC) or ‘Fibre-Reinforced Plastics’ (FRP) or simply ‘Fibreglass’. Urethane adhesives are the clear market leader in this area, particularly in the automotive industry where their resilience and resistance to peel, fatigue and impact have made them the first choice for large area panel bonding; although primers are sometimes needed. Toughened epoxies are used where more load bearing capability is needed. Reactive acrylics have also been shown to be very versatile adhesives for these materials, they can be used without primers and have an excellent combination of rapid curing, resilience and load bearing properties. Cyanoacrylates perform well in small gap situations where ‘instant’ cure is the dominant requirement.

Thermoplastic polyesters include unfilled or reinforced grades of polycarbonates, polyethylene terephthalate, polybutylene terephthalate and blends and copolymers of these plastics. Cyanoacrylates and urethanes bond well to these materials. UV-cured acrylics are suitable for transparent plastics like polycarbonate. Silicones can be designed with internal adhesion promoters to bond to specific polyesters.

Styrenic thermoplastics include polystyrene itself, acrylonitrile-butadiene-styrene terpolymers (ABS) and plastic blends such as polyphenylene oxide/styrene. Most adhesives can be used to produce strong bonds with these plastics but primers and solvents should be tested carefully for solvent attack or cracking.

Polyvinyl chloride (PVC), often referred to as simply ‘vinyl’ comes in rigid and flexible forms. The latter, which is heavily plasticised, can often cause bonding problems because of the plasticiser exuding into the bondline. PVC is often solvent-welded. Cyanoacrylates and reactive acrylics are usually suitable for both rigid and flexible versions but testing is essential. Silicones can often be used successfully on rigid PVC.

Acrylic plastics such as polymethylmethacrylate are sometimes solvent welded. Acrylics, urethanes and cyanoacrylates are good adhesives but stress cracking can occur with highly-stressed parts. Specially formulated silicones work well too.

Acetals, often used for their lubricating properties and chemical inertness, can be quite difficult to bond. Abrasion or chemical surface treatment increases the strength. Hot melts give fair bonds and new coupling agents allow very good bonding with cyanoacrylates.

Polyamides (Nylon) can be bonded well with cyanoacrylates, epoxies, hot melts and acrylics. Careful durability testing of joints is recommended because of the tendency of the plastic to absorb atmospheric moisture.

Adhesives are a very versatile method of joining plastics. They offer the design engineer tremendous scope in materials selection, joint design, processing and cost savings.

However, just as there is no universal plastic for every application, there is no universal adhesive. Treating the bonding process as an integral part of the entire design and assembly operation, coupled with thorough evaluation and testing of all the individual components of the system will ensure optimum performance and cost-effectiveness.

Companies like Permabond and Henkel-Loctite publish excellent guides to bonding specific plastics.

### 6.3.4 Bonding of Non-Polar Plastics

When attempts are made to bond certain plastics such as polyethylene, very weak assemblies are obtained with tensile shear strengths of less than 0.7 MPa (100 psi) and which readily fail under slight impact or exposure to moisture.

Typical low surface energy polymer substrates include plastics such as polyethylene, polypropylene, fluoroplastics like polytetrafluoroethylene (PTFE), polyolefin/rubber composites and the so-called thermoplastic polyolefins (TPOs). These polymers are of considerable interest to the design engineer because of their desirable properties, for example, the chemical and heat resistance of PTFE and the low cost and easy mouldability of polyolefins.

The polyolefins, polyethylene and polypropylene, are of considerable commercial importance and copolymers and blends with rubbers have become very important as thermoplastic polyolefins (TPOs). There has also been a large increase in use of these plastics in both interior and exterior applications in the automotive industry. Polyolefins are relatively low cost thermoplastics, easy to mould or extrude and have good mechanical properties coupled with good resistance to chemicals and excellent weather resistance.

However, the utilisation of polyolefins in many applications has been severely limited by the extreme difficulty of assembling them in a fast and cost effective way.

Polyolefins and fluoroplastics are difficult to bond for several reasons:

- Low surface energy – a prime requisite for successful adhesive bonding is successful spreading and wetting of the adhesive on the substrate. In order for this to be achieved, the substrate must have a high enough surface energy to overcome the surface tension forces in the adhesive. Table 6.4 shows critical surface tensions of plastics. Note that polyolefins and fluoroplastics have very low surface energies.

<b>Table 6.4 Critical surface tensions of plastics</b>	
<b>Material</b>	<b>Critical Surface tension (Dynes cm<sup>-1</sup>)</b>
Polyethylene	31
Polypropylene	29
PTFE	18
Polyvinyl chloride	39
Polystyrene	35-37
Nylon 6	46
Polyethylene terephthalate	41-47
Polymethyl methacrylate	39
Polycarbonate	46

- Low porosity – there is no opportunity for the adhesive to penetrate into the plastic and give mechanical interlocking.
- No functional groups – polyolefins are comprised entirely of carbon and hydrogen atoms and are very non-polar polymers. Most adhesives contain oxygen, nitrogen and other electron-rich atoms and are polar materials. Also, the carbon and hydrogen atoms in polyolefins are very unreactive towards many chemicals, thus precluding adhesion through chemical reactions.
- Surface weaknesses – polyolefins usually have broad molecular weight distributions and the low molecular weight molecules tend to migrate to the surface. These low molecular weight

molecules have low tensile strengths and effectively produce a weak boundary layer. Another common problem is the presence of mould release agents on the surface that must be removed prior to adhesive bonding.

The following technologies represent the current state of the art in the bonding of low energy polymer substrates:

#### *6.3.4.1 Thermal Methods*

Flame treatment is widely used to prepare polyolefin surfaces for adhesive bonding, particularly in labelling operations. This method is purported to burn-off contaminants and weak boundary layers and also produces surface oxidation. Although flame treatment can be readily automated on a container labelling line it is very impractical for most product assembly operations.

Polyolefins are thermoplastic polymers that can be easily melted and several welding techniques can be utilised successfully to give strong bonds. These include spot welding, ultrasonic welding, ultrasonic staking, vibration welding, spin welding, hot plate welding and hot air staking. All these methods can be successful but often have severe limitations such as high capital requirements, restrictions on part geometry, inability to bond dissimilar materials or slow production cycles.

#### *6.3.4.2 Chemical Surface Treatment*

The chemical modification of low energy polymer surfaces is carried out typically by treatment with metallic sodium complex dispersions (for fluoroplastics), chromic acid etching, bleach/detergents, potassium iodate/sulfuric acid and other mixtures.

Pretreatment with oxidising acids can increase the adhesive strengths of polyethylene bonded with epoxy adhesives by as much as 600% [13, 14]. Surface analysis of treated specimens indicates the generation of functional oxygen-containing groups, i.e., hydroxyl, carbonyl and carboxyl.

Treatment of PTFE with sodium complexes also gave strong evidence of surface oxidation and results in up to 10-fold increases in bond strength with epoxy adhesives [15].

Although bond strengths can be improved significantly by these chemical methods, they are time consuming, expensive and inconvenient in high volume production situations. There is also the problem of disposing of hazardous waste from these processes.

#### *6.3.4.3 Plasma Treatment*

The gas plasma treatment of plastics involves exposing the plastic to a gas activated by radio frequency energy. Materials exposed to this 'cocktail' of ions, electrons, free radicals and ultraviolet energy are cleaned and made receptive to adhesives. Oxygen plasma treatment of polyethylene appears to remove weak boundary layers and oxidise the surface leading to several-fold increases in bond strength with adhesives such as urethanes and epoxies.

Ammonia plasma treatment of polyethylene gives strong bonds with cyanoacrylate adhesives coupled with excellent strength retention upon water immersion [16]. It is argued that covalent bonding between the surface amine groups and the cyanoacrylate is more resistant to the water than physical bonding alone.

Gas plasma is a relatively clean process with no hazardous by-products and can be automated, although capital and operating costs are high.

#### 6.3.4.4 Other Surface Treatments

The fluorination of polyolefins is a well-established, though expensive, batch process, often used to treat containers to give resistance to hydrocarbon solvents. Kranz and co-workers [17] have reported that fluorination of polypropylene and polyethylene gives a six-fold increase in peel strength when bonded to steel with a two-part epoxy adhesive. Evidence is presented which indicates covalent bond formation between the fluorinated surface and the amine component of the epoxy hardener.

Other treatments that have been reported to enhance adhesion of polyolefins are: contact with phosphorus trichloride in combination with UV radiation [18], electrical discharge [19] and excimer laser treatment [20].

#### 6.3.4.5 Polymer Modification

Several attempts have been made to dramatically alter either the surface or bulk properties of polyolefins in order to increase the surface energy or make them more polar.

Several studies deal with grafting of polar monomers to the polyolefins. The photo grafting of methacrylic acid, acrylic acid, acrylamide and methacrylamide onto polyethylene indeed gave polymers with improved adhesive strength [21], although a distinct trade-off was that the bond lines became hydrophilic and more susceptible to degradation by water.

Other approaches have been to graft itaconic acid to polypropylene [22], acrylic acid to polyethylene after corona treatment [23], maleic anhydride to polypropylene [24], acrylamide to polypropylene after electrical discharge treatment [25], and the bulk heterogeneous grafting of methyl methacrylate onto polypropylene powder [26].

All these studies claim significant improvements in bond strengths although most of the treatment procedures would be extremely cumbersome to carry out on a commercial scale.

#### 6.3.4.6 Surface Primers

All methods of pretreating or modifying low energy polymers prior to bonding are inconvenient, time consuming and often expensive. The use of a surface primer, although still somewhat inconvenient, is a much more desirable alternative which can be used on a production line.

The cyanoacrylate ‘instant adhesives’ or ‘superglues’ are widely used in product assembly operations worldwide because of their one-component nature, speed of cure and versatility. However, like most other adhesives, low strength on untreated polyolefins has precluded their use in many operations. A significant breakthrough was the discovery by Loctite Corporation that certain surface primers can give considerable enhancements to adhesive strength [27]. These primers are not used to pretreat the polyolefins but are simply sprayed or brushed on to the substrate prior to applying the adhesive. In fact they are used in the same manner that the well-known organosilane primers are used to enhance the adhesion and durability of silicones or epoxies to difficult surfaces. Dilute solutions of trialkyl amines, trialkylammonium carboxylates, tetraalkylcarboxylates or ethylene diamine derivatives are applied to polypropylene or polyethylene substrates and the solvents allowed to evaporate. The substrates are then assembled with cyanoacrylate adhesive. All primers give increased bond strengths and the trialkylammonium carboxylates give bonds so strong that failure occurs in the polyolefin substrates (shear strengths of over 7 MPa (1000 psi) are consistently obtained).

Other companies have discovered primers that behave in a similar manner with cyanoacrylates. Henkel [28, 29] has patented the use of imidazole derivatives and claims that bond strengths increase the longer the primer is left in contact with the substrate, prior to application of the adhesive, in contrast to earlier primers.

Toa Gosei [30] has covered primers comprising solutions of imidazole compounds in combination with chlorinated polypropylene or methylmethacrylate/chloroprene copolymers. Koatsu Gas [31] has patented solutions of triethylphosphine and tri-*N*-propyl phosphine.

Although Loctite and the other companies clearly demonstrated the efficacy these primers, the underlying chemical or physical reasons for their usefulness are not clear, beyond the fact that Loctite found that the wetting of the adhesive on the substrates is not affected by the presence of the primer.

University researchers [32] have studied the interaction between solutions of two primers, viz., triphenyl phosphine and cobalt acetylacetonate, and polyolefin surfaces, in order to better understand why these primers promote adhesion using cyanoacrylates. These primers produce bonds that exceed the strength of the plastics and also have good resistance to immersion in hot water. The dependence of adhesive performance on the solvent, primer thickness, age of the primed surface and the durability of the bond were explained by a model where the primer dissolves in the surface of the plastic and facilitates interpenetration of the cyanoacrylate. The primer initiates polymerisation of the cyanoacrylate leading to entanglement of the polycyanoacrylate and polyolefin chains. A significant finding in this work was that maximum performance is obtained when solvents for the primers are chosen which will both wet out on and swell the polyolefin. Such solvents have solubility parameters close to that of the polyolefin and critical surface tensions lower than the polyolefin.

Further credence is lent to this interpenetration theory when a similar effect was observed using a free-radically cured acrylic adhesive system [33]. In this system the primer consisted of a solution of a copper (II) salt and the adhesive was based on methyl methacrylate monomer with a small amount of trifunctional monomer and a hydroperoxide/amine based cure system. It was found that bonds formed on low density polyethylene result in substrate failure and that an interphase of mixed adhesive and polyethylene is formed up to 1.5 mm thick.

3M have recently introduced two-part acrylic-based adhesives that can bond many low surface energy plastics, including many grades of polypropylene, polyethylene and TPOs without special surface preparation. These adhesives are supplied in two-component cartridges or syringes and used with a static mixer. 3M's data (Table 6.5) indicates a very versatile, tough adhesive system with good tensile shear strengths on a wide range of substrates plus peel strengths of 28-32 N/cm (16-18 pli).

**Table 6.5 3M data on their structural two-part acrylic adhesives**

Substrate	Overlap tensile shear strength		Failure mode
	psi	MPa	
Extruded PE	1000	6.9	Substrate
Extruded PP	1040	7.2	Substrate
UHMWPE	770	5.3	Substrate
LDPE	330	2.3	Substrate
ABS	970	6.7	Substrate
Polycarbonate	850	5.9	Substrate
PMMA	810	5.6	Substrate
Rigid PVC	1540	10.6	Substrate
Polystyrene	550	3.8	Substrate
Nylon 6,6 (30% glass filled)	825	5.7	Cohesive
FRP	2370	16.3	Cohesive
Galvanised steel to PE	985	6.8	Substrate (PE)
Steel to PE	970	6.7	Substrate (PE)
2024 Aluminium	2150	14.8	Cohesive
Oily steel (galvanised)	2150	14.8	Cohesive



Based on 3M patents [34, 35] and their material safety data sheets, these adhesives appear to have one-component comprising an amine-complexed organoborane initiator, which is extended with a polyester adipamide and a second component comprising a toughened methacrylate monomer system. Organoboranes have been known for many years as initiators promoting adhesion to low-energy surfaces but have been difficult to handle. 3M appear to have overcome these problems. Polyfunctional aziridines are also components of these systems, an area where 3M have patent literature on their use as primers for polyolefin surfaces.

The major limitation of these adhesives appears to be their cure time, with time to reach handling strength being 2 to 3 hours at room temperature and full cure in 8 to 24 hours – although heat can accelerate the reactions. Increasing the cure speed of these systems without losing their beneficial properties is an area of current research activity. This is an exciting piece of technology with much potential for the future.

A pioneering Ohio company, called Silicone Solutions ([www.siliconesolutions.com](http://www.siliconesolutions.com)) has recently introduced fast curing RTV silicone adhesive/sealants that they claim have excellent primerless bonding to a wide range of plastic including polyolefins. No further information is available on the patent-pending technology, beyond that it uses new crosslinking technology.

#### **6.3.4.7 Conclusions**

Although the ultimate goal of preparing a single component adhesive that will bond low energy surfaces such as polyolefins has not yet been reached, significant advances have been made, particularly in the area of cyanoacrylates and acrylics. With the explosive growth in the use of polyolefins, driven by their low cost and new metallocene catalysts that can produce ‘tailored’ properties, we can expect much future research activity in this subject.

### **6.4 Bonding of Wood**

Wood is bonded for both exterior and interior applications in the construction and furniture industries. In exterior applications, durability against water and weather is the key property required of an adhesive, whereas for interior applications, factors such as cost, ease of use, colour and lack of staining are often important factors in addition to performance. Wood must also be bonded, not only to itself, but also to a wide range of other materials such as metals and plastics, particularly in the furniture industry.

Historically, adhesives for wood came from natural products – casein adhesives from milk, starch adhesives from corn, and animal blood adhesives but all have been replaced by synthetic adhesives.

The mechanisms for the bonding of wood with adhesives have not been fully evaluated but appear to involve a combination of mechanical interlocking of the adhesive in the pores of the wood coupled with molecular attraction. Because of the preponderance of hydroxy groups in the cellulosic nature of wood, it also seems likely that condensation of these groups takes place with common wood adhesives to form covalent bonds.

Pressure is usually applied during wood bonding and this aids in penetration of the adhesive into the pores and cells of the wood. The strength of bonds to wood increases as the density of the wood increases at low densities (less failure of the wood at higher densities), but at very high densities, wood becomes more difficult to bond, presumably because of less penetration of the adhesive.

Synthetic wood adhesives are best categorised as thermosets and thermoplastics:

Thermosets	Thermoplastics
Phenol-formaldehyde	Thermoplastic hot melts
Urea-formaldehyde	PVA emulsions
Melamine-formaldehyde	Polychloroprene cements
Isocyanates	Rubber adhesive sealants
Epoxies	Cyanoacrylates
Thermoset urethanes	Crosslinked emulsions

Phenol-formaldehyde (PF) adhesives are the leading adhesives for the production of exterior grade composite wood products such as plywood and oriented strand board. Bonds made with PF resins are stronger than the wood under long-term outdoor ageing.

Urea-formaldehyde (UF) is a much lower cost adhesive than PF and is used predominantly in the production of medium density fibreboard for interior use. It degrades rapidly under moist conditions and is not used for exterior applications.

Melamine-formaldehyde (MF) adhesives are more expensive but are almost as good as PF adhesives for exterior applications.

Isocyanates are the basic chemicals used to make polyurethanes where they react with polyols to form the urethane linkage. Bayer the leading European producer of isocyanates has pioneered the use of methylene diphenyl diisocyanate (MDI) to manufacture composite wood products.

Diisocyanates are highly reactive chemicals that develop strong and durable bonds to wood presumably through reaction with water and the hydroxyl groups in wood.

Epoxies are two-component adhesives that cure and crosslink after mixing to produce strong, rigid durable bonds to wood, that have good resistance to weathering. They are particularly effective for bonding metals to wood, where PF, UF and MF adhesives have poor performance.

Thermoset urethanes can be two-component mixable systems or one-component systems cured with atmospheric humidity. They are highly effective adhesives for the production of structural insulated panels where a sandwich of expanded polystyrene between two panels of oriented strandboard is made.

Crosslinked emulsions are two-component adhesives comprising a polyvinyl acetate or acrylic emulsion crosslinked with an isocyanate. They are used for durable wood panel bonding and are also approved for the construction of structural insulated panels.

Thermoplastic hot melts such as EVA are not used in structural applications where high strength is required but are commonly used in the furniture industry to attach decorative materials such as edge banding to panels and table tops and for wrapping of profiles. They are low cost adhesives whose application can be readily automated – edge banding, for example, is done on machines where routing is done immediately after bonding. Higher cost hot melts such as polyamides can be used where higher performance or better heat resistance is required.

PVA emulsions are the most common low cost adhesives used by wood workers and the furniture industry for bonding joints or enhancing the strength of nailed or screwed assemblies. They are sold as liquid products containing 50-60% solids and set rapidly at room temperature to give high strength bonds. However, their moisture resistance is poor and loaded joints tend to creep, particularly at elevated temperatures. Moisture resistance can be improved by copolymerising with acrylic monomers or adding catalysts to cause crosslinking, but at increased costs.

Polychloroprene contact cements, both solvent based and emulsions, are used for laminating countertops in the furniture industry. The elastomeric nature of these adhesives makes them very effective in providing strong bonds to highly stressed joints. The solvent based versions were also commonly used for foam bonding but have been replaced by latex and sprayable hot melts because of solvent emission regulations.

Rubber adhesives and sealants are solvent based or latex adhesives based on low cost rubbers such as SBR, and are used in the construction industry for attaching and sealing panels to floor joists and wall frames. They are not high strength adhesives but fill large gaps, are very flexible and provide good sealing properties.

Cyanoacrylate instant adhesives bond well to some woods but the acidic nature of some wood species cause very slow curing. Special wood bonding versions of these adhesives have been prepared and the major use is probably for bonding balsa wood in the assembly and repair of model aircraft. Table 6.6 shows the properties of wood adhesives.

<b>Table 6.6 Properties of wood adhesives</b>			
<b>Type</b>	<b>Strengths</b>	<b>Weaknesses</b>	<b>Typical applications</b>
Phenol-formaldehyde	High dry and wet strength, very durable under wet conditions	Red colour, cured at high temperatures for long times	Major adhesive used for exterior plywood, OSB and hardboard
Urea-formaldehyde	Low cost, light colour, good strengths	Poor durability under wet conditions	Interior plywood, fibreboard, particleboard, furniture cores
Melamine-formaldehyde	Very durable under wet conditions, light colour. Faster curing than phenolics	Expensive, not as durable as phenolics	Bonding of structural lumber and plywood
Isocyanates	Easily spray applied, high strengths, bond to plastics and metals	Need high temperatures and pressures for best strength, toxic and irritant fumes	Flakeboards, OSB
Epoxies	High strength, room temperature cure, fills large gaps, bond to plastics and metals, low colour	Two-component, expensive, limited durability under wet conditions	Assembly of lumber in boats and aircraft General purpose home and woodworking adhesive
Thermoset urethanes	Cure at room temperature, bond to plastics and metals, low colour	One-component is slow curing. Two-component has short pot life	Structural insulated panels
Crosslinked emulsions	Low cost, room temperature cure, good durability	Two-component, short pot life	Structural insulated panels
Thermoplastic hot melts	Very fast setting, low cost	Expensive application equipment, poor high temperature resistance and resistance to creep	Edgebanding and profile wrapping in furniture construction
PVA emulsions	Low cost, one-component, cure at room temperature	Poor high temperature resistance and resistance to creep	Furniture laminating, panelised wall and floor systems
Polychloroprene cements	One-component, fast drying, very flexible	Expensive, flammable toxic solvents used.	Laminate bonding
Rubber adhesive sealants	Low cost, very flexible, good gap filling	Poor adhesive strength, limited durability under wet conditions	Internal construction such as floor and wall installation
Cyanoacrylates	One-component, fast curing	Expensive, no structural capability, poor moisture resistance	Bonding of models, particularly balsa wood aircraft

## 6.5 Comparison of Sealants

Although sealants are used in industrial and automotive applications where fluid and temperature resistance are key properties, most sealants are used in the construction industry for either interior or exterior applications.

Most interior sealing is for air sealing with the exception of bathroom caulks and plumbing sealants. When selecting an interior sealant, properties like colour, odour, drying time, paintability, and resistance to mould are important characteristics.

Exterior sealing is used for weatherproofing rather than air sealing. An exterior product must endure more thermal and environmental stress. Curing time is not usually as important but joint movement capability, UV resistance and overall weatherability are important characteristics.

The design of a sealing system involves more than choosing the sealant with the right physical and chemical properties. The design of the component to be sealed, the performance expected of the sealant, the expected life of the finished product, and the practical and economic consequences of using a particular product must all be considered in selecting the best sealant.

Klosowski [6] has published a checklist for sealant selection (Table 6.7) and has classified sealants as low, medium, and high range in terms of joint movement capability – a key property for any type of building sealant (see Table 6.8).

Table 6.7 Checklist of considerations for the selection of construction sealants	
Required joint movement Minimum joint width Required strength Chemical environment In service temperatures Temperatures at time of application Intensity of sun and weather in service Longevity General climate at application time Materials cost, initial and lifetime Installation cost	Other: Fungicides Radiation resistance Insulating or conductive requirements Colour Intrusion or abrasion resistance Cure rate Below-grade or continuous water immersion Accessibility of joint

Table 6.8 Categorisation of construction sealants		
Range	Examples	Characteristics
Low	Oil-based, vinyl latex, butyl, bituminous	JMC $\pm$ 3%, service life 2-10 years, low cost
Medium	Acrylic latex, solvent acrylics, butyl, polychloroprene	JMC $\pm$ 5% to $\pm$ 12.5% service life 5-15 years, medium cost
High	Polyurethanes, polysulfides, silicones	JMC $\pm$ 12.5% to +100/-50%, service life 10-50 years, high cost
JMC = joint movement capability as % of joint width + = expansion - = compression		

Table 6.9 shows general characteristics of several types of sealants.

<b>Table 6.9 Properties of construction sealants</b>					
<b>Type of sealant</b>	<b>JMC (%)</b>	<b>Life span (years)</b>	<b>Strengths</b>	<b>Weaknesses</b>	<b>Typical applications</b>
Oil-based	±2	3 to 5	Low cost	Dries hard, cannot be painted	Interior rigid joints
Vinyl acrylic latex	± 2	8 to 10	Low cost, paintable	Very poor flexibility and UV resistance	Good general purpose interior sealant
Acrylic latex	± 5% to ± 12.5	5 to 15	Fairly flexible, paintable, fair weatherability, fast drying	Moderate JMC	Moderate cost interior and exterior sealant for low movement joints
Solvent based rubber	±12.5	10 to 20	Fairly flexible, paintable, good weatherability	High shrinkage	General purpose exterior sealing
1-part polysulfide	±12.5 to ±25	15 to 20	Very low MVTR, fuel resistant	Very slow curing, expensive	Large joints, masonry and concrete
2-part polysulfide	±25	15 to 20	Very low MVTR, fuel resistant	Expensive	Joint filler
Solvent based butyl	±5 to ±10	5 to 10	Very low MVTR, very flexible, paintable	High shrinkage, slow curing	Exterior metal and masonry sealant, insulated glass.
Polyurethane	±25	10-20	Flexible, good abrasion resistance	Not for use on glass, poor UV resistance	General exterior non-glazing applications
Silyl-terminated polyether	±25	10 to 20	Paintable, non-staining, good low temperature properties	Not for use on glass, poor UV resistance	General exterior non-glazing applications
RTV Silicone	+100, -50	20 to 50	Best flexibility, waterproof, best durability	Expensive, slow curing, limited depth of cure, can't be painted, high MVTR	Structural glazing, high performance exterior sealing
JMC = joint movement capability MVTR = moisture vapour transmission rate					

There are many federal, military and industrial specifications and standards for sealants [37].

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## **7 Applications and Markets for Adhesives and Sealants**

### **7.1 Packaging and Labelling**

Packaging is the largest single market for adhesives if we include the construction of corrugated and paperboard. The three most important uses of adhesives in packaging include corrugated box manufacturing, film lamination and label attachment. There has been a great deal of growth in packaging adhesives in recent years and this is expected to continue as developing countries use more packaging to prevent spoilage of food during distribution.

Packaging adhesives can be subdivided by technology and chemistry as follows:

- Solvent-borne dry bond adhesives
- Water-borne dry bond adhesives
- Solvent-borne pressure-sensitive adhesives
- Water-borne pressure-sensitive adhesives
- Wet bond adhesives
- Hot melts
- Liquid adhesives (100% solids)
- Energy curable adhesives – ultraviolet (UV) and electron beam (EB)
- Cohesives.

Dry bond adhesives are applied from solvents or water, dried by heating and airflow and then activated, typically using a heated nip roll. Typical technologies are polyurethanes or acrylics.

Pressure sensitives are used predominantly for labelling applications and use rubber or acrylic technology.

Wet bond adhesives are used primarily on paper-based substrates and can range from starch products for corrugated bonding and casein glues for labelling, to polyurethanes and acrylics for more demanding plastics labelling.

Hot melts are used for carton closing and as adhesives for high-speed wrap-around labelling of cans and bottles.

Liquid (100% solids) adhesives for laminating applications are mainly polyurethanes, made by moisture curing of isocyanate-terminated prepolymers or supplied as two-part systems.

The first generation liquid adhesives were one-part polyurethane moisture curing products. They offered high green strength and viscosity but required high bonding temperatures, water-misting equipment to facilitate adhesive reaction and could release unacceptable levels of isocyanates.

The second generation were two-part polyurethanes. They had the advantage of consistent and rapid cure rates and lower application temperatures, but suffered from low initial bond strength and high residual isocyanate levels.

The third generation were improved in terms of application temperatures and residual isocyanate levels.

Fourth and fifth generation products have further improved on residual isocyanate levels. These include both polyurethane and acrylics. Polyurethanes tend to be used for the more demanding applications and acrylics for less stringent applications.

Energy curable adhesives include both ultraviolet (UV) and electron beam (EB) cured systems. These low viscosity, 100% solids systems, are based on free radical or cationic curing of acrylic

and epoxy monomers. They are extremely fast curing and very easy to apply, although work needs to be done to minimise residual monomer levels for applications like food packaging. A typical application for UV adhesives is in wrap-around shrink labelling, where conventional thermoplastic hot melts cannot withstand heat stresses incurred during exposure in heat tunnels, leading to creeping of the overlap seam. UV adhesives are crosslinked, leading to much higher heat resistance.

Cohesives (sometimes called cold adhesives) are adhesives that stick only to themselves. They are applied to both substrates being assembled and then pressed together to create a bond. The most common materials used are natural rubber latex and polychloroprene. Cohesives are particularly useful for packaging temperature-sensitive products like chocolate and ice cream.

Adhesives play an integral role in the production of flexible packaging. The main function is to bond two or more substrates together to form a lamination having more useful properties than the sum of its parts. Adhesives, although usually only a small portion of the entire lamination when compared to the wide range of films, foils, papers or printing inks used in flexible packaging, are vital for maintaining the end use properties of a finished package. Adhesives are generally applied in one of the last steps of the converting process and are often given the task of overcoming inherent shortcomings of the other flexible packaging materials.

Among the plastic substrates commonly requiring adhesion in the context of flexible packaging are:

- Polypropylene (PP)
- Oriented polypropylene (OPP)
- Biaxially oriented polypropylene (BOPP)
- Cast polypropylene (CPP)
- Polyethylene (PE)
- High density polyethylene (HDPE)
- Medium density polyethylene (MDPE)
- Low density polyethylene (LDPE)
- Linear low density polyethylene (LLDPE)
- Ultra low density polyethylene (ULDPE)
- Ethylene vinyl acetate (EVA)
- Polyvinylidene chloride (PVDC)
- Polyamide (PA)
- Polyethylene terephthalate (PETP)
- Metallised PETP
- Metallised PP
- Metallised PE
- Cellophane
- Polyvinyl chloride (PVC)
- Polystyrene (PS)

In addition to bonding these polymers, adhesives may be required to bond plastic to another substrate such as paper or metal foil.

Adhesives for flexible laminate packaging applications have to meet some very rigorous requirements. These include:

- Bonds that exceed the strength of the film
- High application speeds
- Excellent heat, water, chemical and UV resistance
- Excellent clarity

- Resistance to delamination between poorly compatible film layers
- Low odour
- Contain non-migrating, non-toxic additives

Typical packaging applications of adhesives are summarised in Table 7.1:

<b>Table 7.1 Packaging applications for adhesives</b>	
<b>Adhesive</b>	<b>Packaging applications</b>
Dry bond adhesives – solvent-borne	Predominate in more demanding applications such as film lamination despite concerns about VOC emissions and environmental caps. Applications include: Boil in bag, retortable, military and medical packaging.
Dry bond adhesives – water-borne	Replacing solvent-borne systems as performance is improved
Solvent-borne pressure sensitives	Labelling, adhesive tapes and films
Water-borne pressure sensitives	Labelling, adhesive tapes and films
Liquid adhesives, 100% solids adhesives	Flexible packaging laminate applications
Hot melts	Can and bottle labelling. Carton closure.
Energy curable adhesives – ultraviolet (UV) and electron beam (EB)	Laminating adhesives – pouches, films
Wet bond adhesives	Applications include: food packaging, set up (collapsible) boxes, overwraps and overlays, labelling, medical and industrial applications
Cohesives	Applications include: medical packaging, food packaging (confectionery, ice cream)

Food packaging is an area where special testing of adhesives is required.

Most adhesives in food packaging applications are only in indirect contact with food, being separated by a barrier layer. However, some applications, such as labels on fruit and heat sellable lids do come in direct contact and all packaging adhesives must meet very strict regulations. For example the US Food and Drug Administration (FDA) has three sections for food adhesives:

- (1) Section 175.05 Adhesives – this contains a list of approved raw materials for adhesives that are separated by a functional barrier from the food.
- (2) Section 175.125 Pressure sensitive adhesives – lists conditions of safe use, and components of adhesives that may be used as the food contact surface of labels and tapes that are applied directly to poultry, dry food and processed, frozen, dried, or partially dehydrated fruits and vegetables. Also lists certain additional substances that may be used as the food contact surface of labels and tapes that may be applied to raw fruits and vegetables.
- (3) Section 175.1390 Laminate structures for use at temperatures of 250 °F (121 °C) and above - this regulation provides conditions of safe use for retort pouches, lists substances that may be used as adhesives in retort pouches and provides specifications for the finished products.

Summary of developments for adhesives in packaging applications:

- Solvent-based adhesives are being replaced by aqueous and hot melt adhesives. New developments in crosslinking systems are accelerating this conversion.

- Improvements in terms of application temperatures and residual monomer levels.
- New hot melts that can be applied at around 120 °C rather than the traditional 175-190 °C.
- UV and electron beam systems will become very important in the future because of the ability to cure fully within seconds, with electron beam systems being favoured because of the absence of photoinitiators, which are possible toxic contaminants in food packaging applications. Capital cost of equipment is a limiting factor with these systems, making them more suitable for high volume users.
- New surface treating techniques such as Openair™ plasma technology (PlasmaTreat Inc., [www.plasmatreat.com](http://www.plasmatreat.com)) are allowing good adhesion to low-energy surfaces such as polyethylene and polypropylene.

The packaging of tobacco to form cigarettes is an important use for adhesives. Various water-based formulations are used. Table 7.2 shows the adhesive ingredients disclosed by Phillip Morris USA and used in filter adhesives and sideseam adhesives.

<b>Table 7.2 Adhesive raw materials used in cigarette manufacture</b>	
<b>Filter adhesives</b>	<b>Sideseam adhesives</b>
Ethylene-vinyl acetate copolymer emulsion	Ethylene-vinyl acetate copolymer emulsion
Polyvinyl acetate	Polyvinyl acetate
Diethylene glycol dibenzoate	Starches and/or modified starches
Dipropylene glycol dibenzoate	Diethylene glycol dibenzoate
Polyvinyl alcohol	Dipropylene glycol dibenzoate
Vinyl alcohol-vinyl acetate copolymer	Vinyl alcohol-vinyl acetate copolymer
Polyvinyl alcohol boric acid complex	Polyvinyl alcohol
Triacetin	Polyvinyl alcohol/boric acid complex
Microcrystalline hydrocarbon wax	Triacetin
Paraffin wax	Microcrystalline hydrocarbon wax
Polyethylene	Processing aids (defoamers, preservatives)
Alpha-methylstyrene polymer	
Hydrocarbon resin – Hydrocarbons, C6-20, Polymers, hydrogenated	
Hydrocarbon resin – ethenylbenzene, copolymer with (1-methylethenyl) benzene	
Microcrystalline wax	
Styrene, limonene copolymer	
Boric acid	
Processing aids (defoamers, preservatives)	

## 7.2 Construction

Including wood resins, construction is by far the largest segment for adhesives worldwide.

Large amounts of adhesives are used to manufacture building materials, such as plywood, structural flakeboards, particleboards, fibreboards, structural framing and timbers, architectural doors, windows and frames, garage doors, factory-laminated wood products and glass fibre insulation. Adhesives are used in smaller amounts to assemble building materials in residential and industrial construction, particularly in panelised floor and wall systems. Significant amounts are also used in nonstructural applications, such as floor coverings, countertops, ceiling and wall tile, trim and accessories.

Phenol-formaldehyde resins (PF) for plywood and oriented strandboard (OSB), and urea formaldehyde resins (UF) for particleboard and medium density fibreboard (MDF) are the largest markets for adhesives.

The declining availability of old-growth timber has accelerated the switch to engineered wood products such as particleboard, OSB and MDF. Engineered wood products can use lower quality woods and wood wastes as feedstocks, providing unique advantages over solid timber products.

The non-structural panels industry has addressed the health concerns related to formaldehyde emissions by using re-engineered UF resins that have reduced emissions to one-tenth the level typical of older resins. Non-structural panels continue to grow and have had particular strength due to the popularity of 'ready to assemble' furniture and cabinetry markets. Particleboard overlaid with wood veneer or plastic laminates has been a mainstay for these applications.

Bonding of MDF is the fastest growing segment of the wood panel adhesives market. MDF is beginning to replace traditional particleboard in many applications. The unique properties of MDF – its small particle size and uniform density – allow it to be machined or pressed into complex shapes. MDF applications include construction moulding trim (baseboards, copings) and architectural shapes (pillars, columns).

The urea-formaldehyde adhesives used to bind the wood fibres in particleboard and MDF use a high proportion of formaldehyde in comparison to other resins. Industry forecasts suggest that MDF output will continue to grow.

Plywood has been the traditional structural panel, but the declining availability of high quality veneer timber is accelerating its replacement with cost advantageous products such as oriented strandboard (OSB). OSB uses lower quality and faster growing woods, which are 'waferised' into small chips, combined with a phenol-formaldehyde adhesive and pressed into finished panels. OSB uses approximately twice the amount of phenol-formaldehyde adhesive per board relative to plywood.

A growing market for adhesives is in the construction of structural insulated panels (SIPs) that use a sandwich construction of expanded polystyrene with facings of OSB. The use of these panels is growing at around 40% per year in US residential construction, primarily because of their high insulation properties compared to conventional wood frame construction and the ability to build houses very quickly. Two types of adhesives are used to laminate these panels – moisture cured one-component polyurethanes and isocyanate crosslinked emulsions. In the US, around 900 tons of adhesives are used p.a. for this application.

Flooring and dry-wall products account for a large part of adhesives in the construction market.

Dry-wall adhesives are mainly solvent based so water-based technologies are expected to benefit under environmental regulations against VOCs.

In the production of fibreglass insulation, phenolic adhesives are used as a binder to secure the glass fibres together, as well as to secure the batting to the kraft paper. Recently, some acrylic adhesives have been used for this application because of concerns regarding formaldehyde emissions.

The seams of acrylic and unsaturated polyester countertops can be bonded in place quickly with reactive acrylic adhesives.

## **7.3 Textiles and Carpets**

### **7.3.1 Nonwoven Fabrics**

Nonwoven fabrics, as their name implies, are not woven in the classical sense of textiles but comprise a web or continuous sheet of fibres laid down mechanically. The fibres may be deposited in a random manner or oriented in one direction. The most widely used fibres include cellulose, polyamides, polyesters, polypropylene and polyethylene. The spun fibres, which may be drawn, are laid down directly onto a belt by carding, air-laying or wet-laying.

For over 40 years, until the development of new techniques such as thermal-bonding and hydro-entangled fabrics, almost all nonwoven fabrics required a chemical binder in order to provide any measure of structural integrity. In addition, the binder was called upon to contribute and convey numerous properties that were necessary for the effective performance of the fabric.

For much of this period, binders were essentially the weak element in developing fully acceptable nonwoven fabrics. The fibres that were available to the nonwoven industry were the same fibres that were available to the woven textile and other fibre-based industries; hence, the fibres were fully acceptable.

The deficiencies cited against nonwovens generally were deficiencies attributable to an inadequate binder. Common complaints were:

- The fabric doesn't have enough strength.
- The fabric is too stiff.
- The fabric has inadequate absorbency.
- The fabric shows poor launderability.
- The fabric has inadequate dry cleanability.
- The fabric simply doesn't feel like a textile.

As a consequence, a great deal of research has been done into the continuous improvement of chemical binders. The steady improvements in nonwovens' performance that occurred over a period of many years were, in no small measure, due to improvements in the performance and utility of the binder.

In the very early stages of nonwovens development, different types of natural resins and glues were used to bond nonwovens. While they conveyed some integrity and strength to these webs, they also had many glaring deficiencies. Consequently, synthetic binders were developed to meet the structural and performance requirements of nonwoven fabrics.

Vinyl acetate latex was the first successful synthetic binder used in substantial volume. This material had distinctly superior adhesive properties, strength and performance compared to the early natural adhesives. This binder had considerable flexibility in formulation, and could easily be applied to fibre webs by a variety of application processes, including print bonding.

The industry was faced with the inevitable compromise in fabric properties of nonwovens bonded with synthetic materials. In order to build strength in the fabric, increasing amounts of resin must be applied, which results in more stiffness. If softness was necessary, it could be achieved only by sacrificing strength.

A substantial improvement in this trade-off of strength and softness was achieved with the introduction of acrylic-based latex binders in the 1950s and 1960s. By proper selection of comonomers, it was possible to build improved softness properties with adequate strength. Consequently, these binders became widely used by most of the nonwovens industry, despite a higher cost than VA latex.

As polymer technology for manufacturers of synthetic binder systems improved, a greater variety of chemical building blocks became available with much greater flexibility in terms of binder strength, durability, and other properties. The introduction of crosslinkable and self-crosslinking binder polymers turned out an entirely new range of fabric properties. This was particularly noteworthy in durable nonwovens where such durability features as washability and dry cleanability were important.

Crosslinking is achieved by firstly incorporating small amounts of functional monomers during the preparation of the latex and then carrying out a crosslinking reaction. The main functionalities in binders are carboxyl and amide side chains, produced by using monomers like acrylic acid and acrylamide, respectively. Carboxyl groups are normally reacted with metal oxides or amino resins, whilst pendant amide groups can be reacted with formaldehyde to produce *n*-methylol groups, which condense with themselves to produce self-crosslinking resins.

#### *7.3.1.1 Important Characteristics of Latices for Nonwoven Applications*

The adhesive binders used in the nonwoven industry comprise from 5% to 60% of the weight of the fabric on a dry basis. Thus, they are not merely adhesives but contribute many of the important characteristics to the fabric.

Depending on the end use of the fabric, the binder can influence strength, softness, adhesion, firmness, durability, stiffness, fire retardancy, hydrophilicity, hydrophobicity, antimicrobial properties, organic compatibility, surface tension, dimensional stability, and solvent, wash and acid resistance:

- **Strength:** The strength of a fabric is closely related to the cohesive strength of the applied binder.
- **Adhesion to fibres:** High adhesive strength is very desirable.
- **Flexibility/hand:** Some movement of fibres is often desirable, especially when a soft hand ('feel') is desired.
- **Elastic recovery:** To avoid the permanent deformation of fabric, good elastic recovery is required under strain.
- **Resistance to washing/drying/cleaning:** Many nonwoven products need durability in cleaning processes according to their end uses and latex binders, particularly crosslinked ones, can provide this.
- **Resistance to ageing:** The binder should be stable and not be degraded in the fabric during storage and use.
- **Good colour and colour retention:** Diverse ranges of colours are required, and also colourfastness and yellowing problems should be considered.
- **Hydrophilicity/hydrophobicity:** The type of latex used has a considerable influence on the hydrophilic or hydrophobic nature of the binder. This can affect the wet strength of the fabric as well as its absorbency characteristics.
- **Other:** Flame resistance, resistance to chemicals, air, oxygen, light, heat, etc.

#### *7.3.1.2 Types of Latex Binders*

The following comparison of latex binder chemical types provides an indication of the relative performance, as well as the advantages and disadvantages of each type of binder with particular reference to textile and nonwoven applications. Reference is made to the glass transition temperature ( $T_g$ ) of the base polymer, which is the temperature at which the polymer changes from a rigid solid to a soft deformable polymer and is indicative of the relative softness of a bonded

fabric. Tgs of the most common monomers used in the manufacture of latex polymer for nonwoven binders are shown in Table 7.3.

<b>Table 7.3 Glass Transition Temperatures of Monomers</b>	
<b>Monomer</b>	<b>Tg (°C)</b>
Ethylene	–125
Butadiene	–78
Butyl acrylate	–52
Ethyl acrylate	–22
Vinyl acetate	+30
Vinyl chloride	+80
Methyl methacrylate	+105
Styrene	+100
Acrylonitrile	+130

- Vinyl acetate (VA): The vinyl acetate binders are firm (Tg = +30 °C to +40 °C); however, they are relatively low cost and find extensive use. They offer good dry strength and toughness, but are somewhat hydrophilic and have a tendency to yellow when subjected to heat.
- Acrylic: These binders offer the greatest durability, colour stability and dry/wet performance. Acrylic binders have the widest range of fabric hand properties. They can be formulated to vary from very soft (Tg = –40 °C) to extremely hard (Tg = 105 °C). These binders can be used in virtually all nonwovens applications, although they tend to be expensive. These polymers can be made to crosslink, with substantial improvement in durability.
- Styrenated acrylics: These are tough, hydrophobic binders. The resulting textile hand ranges from soft-to-firm (Tg varies from –20 °C to +105 °C). These binders can be used in applications where there is a need for some wet strength without crosslinking. The use of this type of latex binder does involve some sacrifice in UV and solvent resistance.
- Vinyl acrylics: These binders are more hydrophobic than the straight VA binders. They provide excellent toughness, flexibility and better colour stability. They are the compromise between VA and acrylic, and can compete on a cost/performance basis. The hand range is limited to intermediate softness (Tg = –10 °C) to a firm hand (Tg = +30 °C).
- Vinyl acetate-ethylene (VA/E): These latex binders have a (Tg range of –20 °C to +115 °C, which is equivalent to soft ranging to an intermediate textile hand. They exhibit high wet strength, coupled with excellent absorbency. In general, they are less costly than acrylics. They do have a tendency to have more of an odour compared to other binders. They are used primarily in wipes, air-laid pulp fabrics and similar applications.
- Styrene-butadiene rubber (SBR): These binders have an excellent combination of flexibility and toughness. They range in hardness from very soft (Tg = –30 °C) to very firm (Tg = +80 °C). The styrene-to-butadiene ratio (S/B ratio) is the most common method for describing the relative hand resulting from the use of these binders. The higher the styrene content, the firmer the hand. When crosslinked, this class of binder is very hydrophobic and durable. They are affected somewhat by heat and light because of their tendency to oxidise.
- Polyvinyl chloride (PVC): The homopolymer of polyvinyl chloride is a very hard, rigid polymer (Tg = +80 °C). This polymer must be plasticised to provide flexibility and film-forming properties. Normally, the PVC binders used in nonwovens are softened internally by copolymerising the vinyl chloride with softer acrylic monomers. The hand range of most of these polymers is still relatively firm (Tg > +30 °C). Because this type of polymer is quite thermoplastic, it performs well in heat and dielectric sealing applications. This can be an advantage in some uses. Also, the chlorine content of the polymer promotes flame retardancy. This feature is one of the primary benefits of utilising this type of binder. However, the



chlorine also conveys the tendency to yellow upon heat ageing, due to elimination of hydrogen chloride from the polymer.

- Ethylene-vinyl chloride (EVCL): Binders in this class have a slightly broader hand range ( $T_g = 0\text{ }^{\circ}\text{C}$  to  $+30\text{ }^{\circ}\text{C}$ ) without the external plasticisation required of PVC binders. The presence of the chlorine again conveys some flame retardancy. These binders exhibit good acid resistance, fair water resistance, and excellent adhesion to synthetic fibres. There is some tendency to yellow upon ageing. In essence, this is an internally plasticised PVC binder, considering the ethylene monomer to be the softener.

### *7.3.1.3 Manufacturing of Nonwovens*

Bonding is generally carried out as an integral part of the formation of the nonwoven web. In some fabric constructions, more than one bonding process may be used to enhance physical or chemical properties.

The common methods of bonding include saturation, foam, spray and print bonding:

- Saturation bonding – Saturation bonding is carried out by totally immersing the web in a binder bath or by flooding the web as it enters the nip point of a set of pressure rolls. Excess binder is removed by vacuum or roll pressure.

Drying and curing may be carried out on steam-heated drying cans or in air ovens or perforated-drum dryers. Binder addition levels range from 20% to 60%. Advantages of this method are simplicity, controllable tensile strength and softness by choice and amount of binders. The disadvantages are the great influence of binders on softness, and the limitation in loftiness.

- Foam bonding – Foam bonding is a means to apply binder at low water and high binder-solids concentration levels. The basic concept employed involves using air as well as water as the binder diluent and carrier medium. Foam bonded nonwovens require less energy in drying, since less water is used. The foam is generated by introducing air into the formulated latex while mechanically agitating the binder solution. With the addition of a stabilising agent to the binder solution, the foam can resist collapsing during application and curing, and the bonded fabric will exhibit enhanced loft, hand and resilience. The advantages include less energy required to dry the web, less binder migration and controllable softness by choice and amount of binders. The disadvantages are difficulties in controlling the process and obtaining adequate foaming.
- Spray bonding – In spray bonding, binders are sprayed onto moving webs. Spray bonding is used for fabric applications that require the maintenance of high loft or bulk, such as fibrefill and air-laid pulp wipes. The binder is atomised by air pressure, hydraulic pressure, or centrifugal force and is applied to the upper surfaces of the web in fine droplet form through a system of nozzles. Reversing web direction on a second conveyor and passing the web under a second spray station accomplish lower-web-surface binder addition. After each spraying, the web is passed through a heating zone to remove water, and the binder is cured in a third heating zone.
- Print bonding – Print bonding applies binder in predetermined areas only and is used for fabric applications that require some areas of the fabric to be binder-free, such as wipes and coverstocks. Many lightweight nonwovens are print bonded. Printing patterns are designed to enhance strength, fluid transport, softness, hand, absorbency and drape. Print bonding is most often carried out with gravure rolls. Binder addition levels are dependent on engraved area and depth as well as binder-solids level. Increased pattern versatility can be achieved with the use of rotary screen rolls. Drying and curing are carried out on heated drums or steam-heated cans.

There are two types of printers: rotary screen and rotogravure printers. Binders are applied through a hollow applicator roll in a rotary screen printer, while in a rotogravure printer they are applied by an engraved applicator roll. The main advantage is that outstanding softness of nonwoven fabrics with adequate strength can be achieved.

#### **7.3.1.4 Applications for Latex-Bonded Nonwovens**

Many applications exist for latex-bonded nonwovens, e.g.:

- Wipes and towels
- Medical nonwovens
- Roofing products
- Apparel interlinings
- Filter media
- Coating substrates
- Automotive trim
- Carrier fabrics
- Bedding products
- Furniture applications
- Diapers
- Feminine hygiene products
- Synthetic leather

#### **7.3.1.5 Future Developments in Nonwovens**

In the latter part of the 1970s and 1980s, thermal bonding technology grew rapidly, providing the industry with a realistic method to produce strong and soft nonwoven fabrics without the use of a chemical binder. This development provided substantial advances in performance and properties of many types of nonwovens. One quality of this new bonding technique was that these nonwovens contained no formaldehyde and no chemical additives to cause consumer concern. Naturally, this movement depressed the interest in chemical binders within the industry and has resulted in a decline in binder usage.

Despite this setback, significant improvements and advances have continued to be made by the synthetic polymer industry, to the benefit of the range of nonwoven products that continue to utilise chemical bonding methods. These improvements have involved such developments as formaldehyde-free binders, low-cure temperature binders, complex copolymers with unique characteristics, mouldable binders, and others. In the future, new types of binders may be combined with the present choices, for example, by copolymerisation. Also, new bonding technology may be developed. In addition, new ideas such as reactive binders that can be covalently bonded with fibres, will be continually investigated.

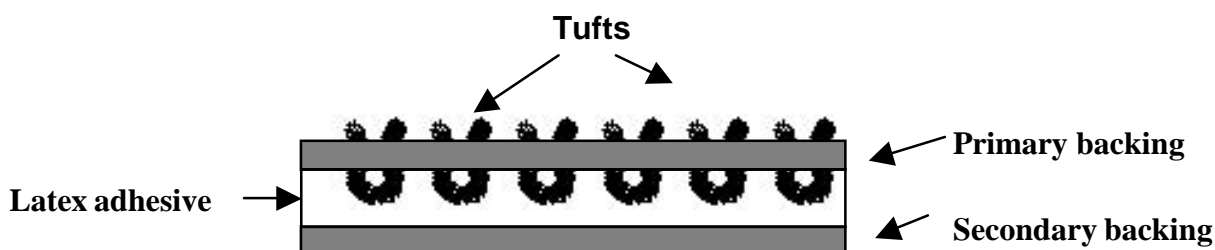
Future demand for latex polymers in the textile and nonwovens market will be driven by such factors as:

- Consumer discretionary income and preferences
- The continued development of speciality niche applications
- Changes in technology in nonwoven products

#### **7.3.2 Carpet Bonding**

Latex adhesives are key components in the production of modern carpets.

Carpet construction methods include weaving, tufting, needlepunching, flocking and knitting. About 95% of the carpet made in the United States is tufted. During tufting, face pile yarns are sewn (or punched) into a primary backing by a wide multineedled machine. Tufts are inserted lengthwise in tufted carpeting, rather than widthwise, as woven carpet is constructed. Tufts are anchored in place with a layer of latex compound, which also attaches the secondary backing (Figure 7.1). The backing layers give the carpet added dimensional stability and strength.



**Figure 7.1 Carpet construction**

The face yarns for carpets are nylon 6 and 6,6, polypropylene and polyester.

More than 95% of the primary backings for tufted carpet are made of polypropylene/olefin (woven and non-woven); occasionally jute and spunbonded polyester primary backing are used.

Secondary backings for tufted carpets are usually jute (nearly 20%) polypropylene/olefin (about 75%) or foam (about 5%). Synthetic backings are resistant to moisture shrinkage. Urethane foam, a newer entry into the backings market, is growing in popularity while latex foam has been losing its share of the market over the past 10 years.

Latex is the product that holds the entire system together by securing the face fibres to the primary backing and then bonding the secondary backing to it. The latex typically comprises 40-60% of the total weight of a carpet.

High styrene-content carboxylated SB latex is the most frequently used backing and laminating compound, although other compounds, such as polyvinyl chloride, amorphous resin, ethylene-vinyl acetate, polyethylene and polyurethane are used. Natural latex is used only on small, washable rugs.

The SB latex is compounded by the carpet manufacturer using calcium carbonate as extender, surfactants to enhance frothability, and polyacrylate thickeners. There are two types of processes used; one is called 'precoat/skipcoat' and the other 'unitary'. The precoat/skipcoat system is the major system for most residential and commercial carpet and involves using the precoat for impregnating and bonding the face fibres to the primary backing and the 'skipcoat' for adhering the secondary backing. The precoat can contain up to 80% of calcium carbonate, is usually frothed for weight control and affects many of the properties of the finished carpet, including piling and fuzzing, hand and strength of tuft binding. The skipcoat contains more latex adhesive and is critical to the dimensional stability of the carpet and preventing delamination of the backing.

The growth of contract floor covering has led to the need for back-coating systems that can withstand high traffic. 'Unitary' systems were developed involving a single layer of specially formulated SB latex with the carpet being glued down.

Carpet bonding accounts for roughly 227,000 tons of total SB latex demand in the US and over 800,000 tons worldwide. Dow's recent acquisition of Reichhold's paper and carpet latex business gives it about 40% of the US carpet latex market. Omnova and BASF account for most of the rest.

Consolidation in the US carpet industry in the late 1990s has led to a situation where the top three carpet manufacturers purchase two-thirds of the SB latex, putting enormous pricing pressures on the latex manufacturers. The manufacturers have responded by focusing on special formulations for specific applications to reduce their dependencies on the commodity latex types.

## **7.4 Consumer**

### **7.4.1 Consumer Adhesives**

The consumer adhesive market includes home repair products, DIY adhesives, craft adhesives and stationery products. It is characterised globally by widespread regional brand recognition of the leading suppliers, but also by a host of private label and low cost products.

Consumer adhesives include:

- Contact cements
- Latex adhesives
- Glue sticks
- Cyanoacrylates
- Epoxies
- Reactive acrylics
- Hot melts
- Adhesive tapes
- Self adhesive notes

Up until the 1970s, consumer adhesives were dominated by solvent based glues and contact cements, sold under such brand names as UHU® in Germany and France, Bison® in the Benelux countries, Bostik® and Evostik® in the UK, and Duco® cement in the US. However, in the US the best-known brand was a polyvinyl acetate emulsion, Elmers® Glue.

Other important regional brands in Europe include Pattex®, Sellotape and Pritt® (all from Henkel), while Scotch® tape from 3M dominates the US tape market.

The consumer marketing of cyanoacrylate instant adhesives in the 1970s revolutionised consumer adhesives in that the rapid fixturing and high strength of these adhesives could be demonstrated readily in a 15 or 30 second TV commercial. These were pioneered by Toagosei with Krazy Glue®, and Loctite with its SuperGlue in the US and Europe. Henkel also has strong brand recognition in Europe with its Sicomet® brand whilst Toagosei uses Cyanolit® in that region.

Loctite tried to establish a global brand with its SuperGlue name, but efforts were derailed when it lost its trademark. This led to the formation of several companies marketing so-called 'Superglues' including SuperGlue Corporation in the US (now part of Pacer Technology). Several hundred million tubes and small bottles of these adhesives are sold worldwide for general purpose repairs and special applications such as artificial nail bonding and model building.

With the increasing global consolidation of the adhesive industry, global branding is certainly possible and the Post-It® self-adhesive notes from 3M are probably the best example. Henkel is also trying to establish global brand names with its Pattex® and Pritt® names. The first Pritt® glue stick for paper entered stores in 1969. Today, the Pritt stick is the market leader, used for gluing in over 120 countries, and Pritt® has become an umbrella brand for a variety of products for sticking, correcting and highlighting. Other companies use regional branding, for example Toagosei is

developing markets worldwide for instant adhesives under brand names of Aron Alpha® in Japan and Asia, Krazy Glue® in North America and Cynanolit® in Europe. GE, well known for its silicone sealants, has recently begun to leverage its brand name for other adhesive and sealant products since its acquisition of Macklanburg-Duncan and the formation of its Sealants and Adhesives business unit.

#### **7.4.2 Consumer Sealants**

Acrylic latex sealants and caulks are the leading DIY product with about 50% of the market in the US. Compared to the well known silicone caulks they are much easier to dispense, can be cleaned up with water and can be readily painted with latex paint. Their major weakness is low flexibility leading to poor joint movement capability. Acrylic, styrene acrylic and vinyl acrylic emulsions are used for formulating both pigmented and clear sealants. Some products have a small amount of silicone added and are marketed as 'siliconised latex'. This generally means that they contain a very small amount of a silicone fluid for better and greater plasticity, or a silane coupling agent for better adhesion, or a silica filler for thickening. A siliconised sealant is close in performance to the parent material with no silicone, silane or silica in it. The most noticeable difference between the siliconised and standard products is usually the very large size of the word 'silicone' on the label.

Latex foam sealant is a relatively new product, sold in aerosol cans similar to the more familiar polyurethane foams. A nozzle-and-trigger assembly is used to squirt wet foam into cracks, gaps, or voids, to seal out drafts, prevent energy losses and keep out pests. The latex material reaches 75% of its total expansion as soon as it is applied, unlike urethane foams that gradually expand more than 200%. This feature prevents latex foam from warping window and door frames where urethane foam might cause distortion. Like urethane, latex foam forms a skin as it dries, which allows for tooling and smoothing. Latex foam, however, can also be shaped or tooled while wet, and stays softer and somewhat pliable even after it is fully cured. Successive layers can be applied if necessary.

Easy clean-up is probably the biggest advantage for using latex foams over traditional foam sealants. Anyone who has tried to remove excess urethane foam from skin, fabrics, walls or floor surfaces will appreciate how much simpler it is to use soap and water, rather than harsh chemical solvents. While the material is also less irritating, gloves and eye protection are still recommended during application. Latex foam will bond to most construction materials, but it does not offer the adhesive qualities of urethane.

### **7.5 Product Assembly**

Product assembly adhesives are used widely in the assembly of a wide range of products in several market segments, including transportation, appliances, electrical and electronic, medical devices, footwear, sporting goods, cameras and optical goods. Most of these adhesives are reactive systems and in general are the highest value-added and profitable systems for the entire adhesives value chain.

#### **7.5.1 Appliances**

Adhesives are used widely in the construction of both small and large appliances. The appliance market requires fastening, joining and assembly of parts made of a wide variety of substrates. Adhesives for these components must withstand heat or cold, deaden sound and absorb vibration.

Adhesives find widespread use in appliance manufacturing applications for structural bonding, cylindrical assembly, threadlocking, flange and thread sealing, thermal management, wire bonding and harnessing, gasketing and sealing. Adhesives can bond a wide range of materials including dissimilar materials, and decrease total manufacturing costs, making possible many appliance designs that would be impossible or cost-prohibitive using mechanical fastening methods.

New applications have developed with the incorporation of more electronic components in appliances and there are continuous demands on adhesive suppliers for higher performing, more cost effective adhesives.

Many appliance applications for adhesives are for the electrical industry for the assembly of motors and pumps, including anaerobic threadlockers, sealants and gaskets. Fast bonding acrylics have had a major impact on improving productivity in these industries.

Anaerobic threadlockers are used widely in appliances for locking of screws to secure against vibration loosening.

Cyanoacrylates are used in refrigerators to bond door handles, shelves and touch-up switches, and attach identification tags on compressor motors. They also find use as instant adhesives in glass to glass bonding of large shelf assemblies inside the refrigerator. Cyanoacrylates are also used for general purpose bonding of switches located on the control panel, to attach rubber pads to the base legs of washing machines and bumpers to the lid.

RTV silicones are frequently used to seal where resistance to heat and flexibility at low temperatures is required. Typical applications include sealing around ovens and stoves and sealing refrigerator doors.

Epoxyes are commonly used as structural adhesives in small appliance applications including bonding hoses onto vacuum cleaners. Most internal parts of air conditioners are metal and UL approved epoxyes are used for bonding.

UV adhesives are used where situations demand time to adjust parts followed by rapid curing. Applications include bonding plastic and metal trim to glass shelves in refrigerators.

Hot melts are commonly used in refrigerators to fill gaps prior to the injection of polyurethane foam insulation, bonding of control panel covers and tub caps on washing machines, tacking wire harnesses, adhering and sealing the hot air conveyor on tumble dryers, and bonding gaskets to the bottom of steel tanks of dishwashers. Another high volume use for hot melts is in the bonding of paper bags for vacuum cleaners.

Pressure sensitive adhesives provide instantaneous bonds and have many applications in appliances. They are used to bond numerous labels and identification tags, assembly of membrane switches, bonding sound and vibration dampening materials, and attaching of die-cut foam parts and gaskets. Acrylic pressure sensitives are the most widely used because of their good temperature resistance and environmental durability.

### **7.5.2 Electrical and Electronic**

Although the term electronic adhesives has become quite fashionable in recent years to denote high tech products directed at the high tech electronics industry, many of the adhesives in this market segment are actually used in the less glamorous electrical industry.

Before the advent of modern electronic devices, adhesives were used and continue to be used in electromechanical devices such as motors, generators, transformers, solenoids and the processing controls of switches, instruments and relays. A major growth area, particularly in the automotive industry, has been the bonding of DC motor components.

Bonding in these motors can be carried out using anaerobics, reactive acrylics or epoxyes. Epoxyes are used where customers are unable to control gaps and their excellent gap filling ability is valuable. In most cases, primer cured acrylic formulations give durable bonding as long as gaps do not exceed 0.5 mm. Dymax Corporation (US) has been the market leader in motor magnet bonding

with their aerobic acrylics. Recent innovations include adhesives that do not contain acrylic or methacrylic acid adhesion promoters, which can cause corrosion and dual curing systems that can be cured with primers or with UV radiation. Motor applications include armature wire strain relief, coil termination, sealing seams, attaching flange to can, bonding commutator to shaft and mounting bearings.

The electronics industry comprises several market segments including computers, telecommunications, automotive, displays, disk drives, memory modules and consumer products.

As the market for reliable electronics has grown over the past two decades, there has been a need for materials that can bond and protect electronic components under the diverse and demanding conditions in which they must function.

Most electronic adhesives are used on printed circuit boards (PCBs) or for bonding silicon chips.

Until the early 1980s PCBs were manufactured using so-called through-hole technology (THT) where the components were placed on the 'components side' of the printed circuit board, wires inserted into holes, and soldered to copper pads on the opposite, 'solder side' of the PCB.

Another major development was surface mounted technology (SMT) using surface mounted devices (SMD).

Surface mounted devices (SMD) are active and passive electronics components without conventional connecting wires. The SMD components can be placed on the 'solder side' of the PCB and their metal caps soldered to the copper pads of the PCB. Therefore, both layers of the PCB can be used as active areas. The SMT technique opened advantages and new applications through miniaturisation of the components and increased reliability.

Several types of adhesives bonding are used in the electronics industry:

- Wire tacking adhesives. Both cyanoacrylates and UV acrylic adhesives can be used to tack wires in place. Cyanoacrylates are applied to the components and then a topical activator is applied by brush or spray to cure the adhesive instantly. UV adhesives achieve the same result and give more heat-resistant bonds.
- Electrically conductive adhesives are used for such applications as bonding lead wire to electrodes, solder paste replacement in the assembly of SMDs, die attachment and repair of conducting paths. Adhesives such as epoxies or acrylics are highly filled (typically 80%) with conductive metal particles. Metals such as nickel and copper cannot be used because of their susceptibility to oxidation. Precious metals such as silver and gold are the conductive elements of choice due to their stability and effectiveness.

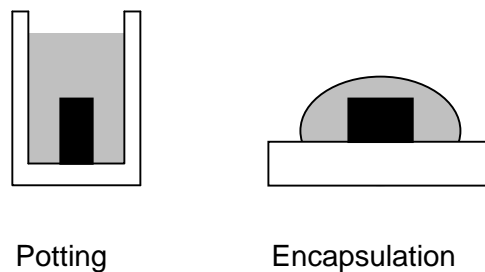
It is possible for silver and gold epoxies to give adhesives with resistivities of  $1 \times 10^{-3}$  to  $1 \times 10^{-4}$  ohm-cm. Silver is most commonly employed due to its cost advantage over gold. In some devices, silver migration may be a problem, and, for these applications, gold is chosen.

Transene Co. (US), is now offering a high bond strength epoxy with silver flake below three microns in each dimension. Reducing the conductive flake size by an order of magnitude has been found to afford manageable, productive bonding for nanotubes, which are projected to be the next possible generation of microelectronic devices.

- Thermally conductive adhesives. Because of the close packing of components on PCBs considerable heat is generated during use and must be dissipated. This is done by attaching heat sinks to the boards. The traditional way of doing this was to use mechanical fasteners with thermally conductive silicone greases to improve conductivity and provide electrical isolation.

However, thermally conductive adhesives have been shown to be an excellent alternative to mechanical fasteners and can be applied rapidly with automatic dispensers. Such adhesives are filled with alumina to provide the thermal conductivity. Surface activated reactive acrylics are good adhesives for this application.

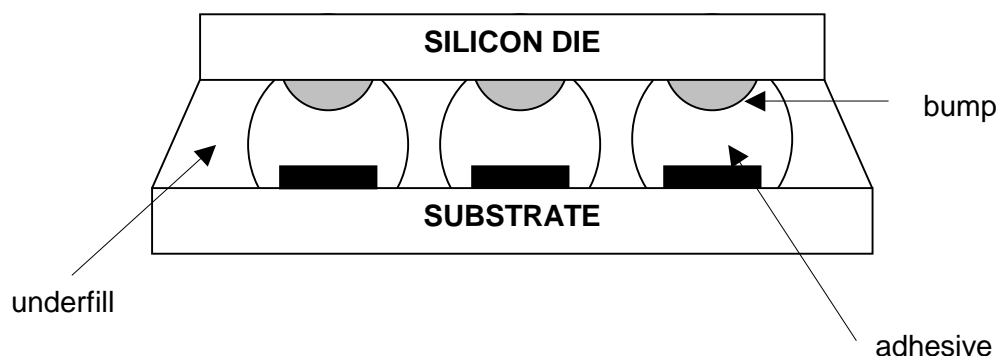
- SMD adhesives or surface mount adhesives (SMAs) are applied for temporary attachment of electronic components on the surface of printed circuit boards during the wave solder or solder reflow processes. A drop of adhesive is applied either on the PCB or under the component and cured quickly, followed by the soldering process. Solder is needed for electrical contact, but is rarely required to withstand shear forces, whereas SMD adhesives give much stronger fixturing of the components.
- Potting compounds and encapsulants. Components on a PCB can be potted or encapsulated. Potting involves enclosing a component in a reservoir and filling with a so-called potting compound. Development of adhesives with controlled flow characteristics can often replace potting with encapsulation, thus removing the necessity for the reservoir. This type of encapsulant is frequently called a 'glob top' adhesive. Figure 7.2 shows potting and encapsulation.



**Figure 7.2 Potting and encapsulation**

- Die attach adhesives. A silicon chip is often referred to as a silicon 'die'. Die attach adhesives are adhesives that are used to bond so-called 'flip chips'. A flip chip is a silicon chip that has balls or 'bumps' of solder on its bonding pads. The chip is then inverted or 'flipped' and bonded to metallisation pads on the substrate (Figure 7.3).
- Flip chip underfill adhesive. In flip chip packages, there is a thermal expansion mismatch between the silicon chip and the alumina ceramic substrate. The coefficient of thermal expansion (CTE) of silicon is much lower than alumina, and large strains are observed in the solder bumps, due to this thermal expansion mismatch. The strain increases as the semiconductor chips are made larger. To compensate for this mismatch, liquid underfill resin having a CTE close to the solder bumps is deposited and cured in the gap between the chip and substrate. The use of underfill adhesives enables structural coupling of the chip and substrate, effectively decreasing the shear stress and thus lowering the applied strain on the solder joints.





**Figure 7.3 Bonding and underfill of a flip chip**

Electronics manufacturers demand high purity and low corrosivity from device components, and adhesives must have very low concentrations of extractable ionics such as sodium, potassium and chloride. Also outgassing of solvents or volatile plasticisers cannot be tolerated.

Epoxy adhesives have traditionally been the materials used in electronic applications because of their high T<sub>gs</sub> that resist high temperature soldering and their excellent environmental durability. They can be heat cured or used as two-component systems. One way of using two-component adhesives is to premix them and freeze the resultant mixture at  $-40^{\circ}\text{C}$  or below in order to prevent curing prior to use. However, they do suffer from long process times and high rigidity that can cause problems in thermal cycling.

Acrylic adhesives have become very important in electronics assembly as demands for increased productivity have increased. UV cured products can fixture or encapsulate components in seconds and can be fully cured in deep sections by heat or by using two-component systems. UV cured silicones are also making entries into potting and encapsulation markets.

In order to meet increasing high temperature demands during processing caused by the future use of lead-free solders, future adhesives will need to be based on very high temperature materials such as anhydride-cured epoxies and bismaleimides.

The global market for electronics adhesives is between \$500 million and \$1 billion according to Henkel estimates in 2001. Impact Marketing Consultants estimated the US market for electronic and electrical products in 1998 at \$160 million and 27,273 tons (Table 7.4).

<b>Table 7.4 1998 US markets for electronics adhesives</b>		
<b>Application</b>	<b>Value</b>	<b>Volume</b>
Electrical and thermally conductive adhesives	\$40 million	1363 tons
Printed circuit applications	\$24 million	4090 tons
Cable sealing	\$18 million	3636 tons
Pressure sensitive adhesives	\$16 million	4545 tons
Motors and magnets	\$12 million	2727 tons
Battery applications	\$8 million	2272 tons
Other applications	\$42 million	8636 tons

Large growth is projected in many electronics applications. For example, global demand for flip chips has grown from 660 million units in 1998 to 2.7 billion in 2002. Computers use 30% of all chips but the wireless phone market is the fastest growing segment.

National Starch is the largest supplier to the electronics market through its Ablestik, Emerson and Cumings and Tra-Con divisions. Henkel-Loctite is also a major player, particularly since the

acquisition of the Dexter-Hysol line of products. Other companies in this field include Epoxy Technology, Bondline Electronic Adhesives, Dymax Corp., Transene and Norland.

### 7.5.3 Medical Devices

Adhesives are essential materials for the modern medical device industry, although overall volumes are small in comparison to other markets.

Mechanical fastening, epoxy adhesives and solvent cements were the traditional assembly methods used when most medical devices were made out of metals, glass and flexible PVC. Epoxy adhesives are still used in the industry, despite their two-component nature and slow curing. Medical device companies still use PVC cements based on solvents such as MEK and cyclohexanone for bonding flexible tubing.

However, with the explosive growth of the medical device industry and the widespread use of a large number of thermoplastic and thermoset plastics, better and faster curing adhesives have become a necessity for performance and productivity reasons.

There are two types of medical applications for adhesives, applications for devices that are outside the body such as instruments, and those inside the body, for diagnostic, monitoring or therapeutic purposes.

Adhesives that are used for devices that may contact the bloodstream need to withstand sterilisation procedures – ethylene oxide, gamma ray or steam autoclaving. For re-usable devices, the ability to pass through multiple autoclaving cycles without losing bond strength is the ultimate test of an adhesive. Epoxy adhesives perform well in autoclave cycles while other adhesives like cyanoacrylates or UV acrylics sometimes lose strength dramatically.

Adhesives used in the medical industry are tested to the USP Class VI or ISO 10993 toxicological classification requirements. This essentially means that the products have been tested by an independent laboratory to verify that they are non-toxic and biologically inert in the cured state. The USP Class VI test method consists of generating extracts of the material in various media and then carrying out acute systemic, intracutaneous and muscle implantation tests on mice or rabbits. ISO Standard 10993 consists of 16 parts. Each part describes specific tests that include a variety of toxicity tests.

The major adhesives used in medical devices (described in Table 7.5).

<b>Table 7.5 Medical device adhesives</b>		
<b>Type</b>	<b>Strengths</b>	<b>Weaknesses</b>
Epoxy	Withstands autoclaving, fills large gaps, long track record in industry	Two-component, slow curing, very rigid, limited plastics bonding
Cyanoacrylate	One-component, very fast curing, low viscosity, high strength on most plastics	Poor gap filling, cannot be autoclaved, blooming, can stress crack some plastics
UV acrylic	One-component, fast curing, bond a wide range of materials	Resistance to multiple autoclaving, cannot be used on opaque substrates, limited gap filling
Polyurethane	Very flexible, bond a wide range of materials	Two-component, slow curing
RTV silicone	Very flexible, withstand autoclaving, bond to low surface energy plastics like PE and PP	1-component versions are slow curing. 2-component require mixing
UV silicones	Fast curing, very flexible, withstand autoclaving	Expensive, limited gap filling

Applications include:

- Bonding of stainless steel needles in glass syringes
- Bonding of stainless steel needles to polypropylene or PVC hubs
- Bonding of catheters and balloons
- Plastic tube assembly
- Potting and encapsulation

Needle bonding has long been a major application for adhesives. The bonding of stainless steel needles in glass syringes that are pre-filled with pharmaceuticals was traditionally done using heat-cured two-component epoxies, but toughened UV acrylic adhesives have led to dramatic increases in productivity with some manufacturers bonding more than a million syringes per day. UV acrylics are also used for bonding disposable syringe needles, where a stainless steel needle is bonded to a polypropylene or PVC hub.

UV acrylics are used to assemble injectors, infusion sets, pressure transducers, drug delivery devices, IV sets, oxygenators, cardiotomy reservoirs, blood heat exchangers, hearing aids, anesthesia masks and blood filters.

Epoxies are commonly used on syringes, endoscopes, catheters, blood heat exchangers, syringes, and dental, surgical and orthopaedic handheld, powered instruments. They are also used in the assembly of stainless steel or titanium access ports that are implanted beneath the skin of patients who require multiple infusions.

Because of cyanoacrylate's low viscosity and speed of cure, it has long been the choice of catheter manufacturers for wicking in and bonding latex balloons to either rigid PVC or polyurethane tubing. Cyanoacrylates are also used to bond components in the assembly of blood pressure transducers, endoscopes, hearing aid subassemblies, IV sets, infusion pumps, orthopaedic devices, cast boots, and diagnostic imaging equipment. Blooming, or the formation of white polymer deposits outside a bondline, can be mitigated by using low volatile cyanoacrylates or by using UV curable cyanoacrylates.

RTV silicones are commonly one-component alkoxy silicones or two-part platinum catalysed addition types. Silicones offer excellent flexibility once fully cured and are particularly useful for bonding of silicone rubber components. Silicones also have outstanding low temperature flexibility and good high temperature resistance and are accepted products for many gasketing and sealing applications.

UV silicones can be cured fully by UV or have a dual cure system where UV does the fixturing and cure is completed by reaction with atmospheric moisture. Applications include tracheal and endotracheal tubes, foley catheters, colostomy devices and chest drainage tubes.

Urethanes are commonly used in potting applications on filters, kidney dialysers, blood heat exchangers and catheters.

A number of medical-grade tapes and films (e.g., single- or double-side coated, woven and nonwoven, elastic and absorbent materials) are available. They are used in a variety of applications, including allergy patch testing, nicotine patches, ostomy devices and general dressings. Acrylic PSAs are the most widely used adhesives for these products. There are many other applications for PSAs in the medical industry including labelling of instruments and attaching surgical drapes.

Hot melt adhesives have potential for use in the medical device industry because of their fast fixturing and relatively non-toxic ingredients. However, most hot melt manufacturers seem to focus their efforts on high volume applications like packaging and woodworking and have not carried out the requisite biocompatibility testing or product development.

Although medical devices is a multibillion dollar industry, the overall volume of adhesives used is quite low. For example, the worldwide market for cyanoacrylates in bonding catheters is only a few hundred kilos. The transdermal patch market is about \$1.6 billion, but adhesives only account for about \$2 million of that.

However, this is a very profitable segment of the adhesive industry with suppliers often getting prices of \$100 to \$300/kg for products.

Important suppliers to this industry include Henkel-Loctite, Dymax, Permabond and manufacturers of pressure sensitive products like Avery Dennison and Adhesives Research.

#### **7.5.4 Footwear**

Adhesives have largely replaced mechanical fastening procedures in the shoe industry such as sewing, nailing and riveting.

Footwear is typically classified into four groups: sports shoes, dress shoes, sandals and vulcanised shoes. Adhesives are used for bonding all parts of the shoes including the outsoles insoles and uppers. Many kinds of materials can be used in footwear manufacturing, including leather, fabrics, rubber, polyurethane (PU), PU coated fabrics, PVC coated fabrics, PVC, EVA rubber, PU and many other synthetic materials.

Adhesives for shoe manufacturing have to be versatile to bond this wide range of materials and also be able to maintain properties under numerous repetitions of bending, straightening, compressing, recovering, rubbing and friction under various climates – rain, snow, wind and fluctuating temperatures.

Toluene-based polychloroprene adhesives were once the mainstay of this industry but have been losing market share to lower cost, higher performing adhesives. There is also considerable environmental and legislative pressure to use safer adhesives.

Most adhesives in the shoe industry are applied by hand or automatically and then later heat-reactivated to form the final bond. This limits the number of technologies that can be used.

The major types of adhesives used are:

- Polychloroprene – A large amount of solvent-base polychloroprene is still used. This type of adhesive is very versatile with outstanding weather resistance. It is till the best adhesive for bonding rubber shoes and boots. Latex versions are available but drying time is longer. Polychloroprene is also very expensive compared to alternative adhesives
- Solvent based polyurethanes - These are based on solvent solutions of hydroxy-terminated polyether polyols and are particularly suitable for bonding sports shoes, many of which are made out of polyurethane. One and a half billion pairs of sports shoes are made annually around the world.
- Polyurethane dispersions - Crosslinkable polyurethane dispersions are becoming alternatives to solvent based systems, albeit with longer drying times.
- Hot melts - Several types of hot melts are used in shoe manufacture, frequently applied in granular or powder form. Copolyamides are used for bonding folded seams in shoe uppers made of leather or synthetic materials. Different melting point resins are used depending on the substrate. EVA hot melts are used for attaching insoles.
- Reactive hot melt urethanes - These adhesives are just starting to be used for high performance applications where their ability to give instant green strength and the cure to give very tough polymers is an advantage.

The global shoe industry uses around 150,000 tons of adhesives per year with over 80% of the production being in Asia.

Major suppliers to the shoe industry include Forbo AG (Switzerland), Donsung (Korean – division of National Starch), H. B. Fuller (US) and Henkel (Germany).

### **7.5.5 Furniture**

Furniture and woodworking is a large market for adhesives.

Common applications include:

- Joints – bonding or reinforcing joints in wood
- Dowels – inserting and bonding a dowel into a predrilled hole in a board
- Drawer wrapping – this is the process of longitudinally wrapping and bonding a flexible film completely around a board, which will be ‘V-grooved’ and ultimately folded into a furniture drawer.
- Face gluing – bonding solid wood components parallel to each other to make a larger board or panel
- Edgebanding and softforming – edgebanding is the process of bonding decorative materials to the edges of various core stocks. Softforming is a similar process, but is applying the edging material to a profiled edge only. Among the more popular edging materials utilised are primed PVC, wood veneers, solid wood, melamine or polyester-impregnated papers, and high pressure laminate. Typical core stocks include particleboard, plywood and medium density fibreboard.
- Profile wrapping – this is the process of wrapping material around preformed profiles. Typical applications are wood veneers to solid or composite profiles, and wrapping a wide range of decorative papers to wood-based and synthetic core stocks.
- Laminating – bonding high pressure laminates to particleboard, medium density fibreboard or plywood to make countertops.
- Foam bonding – bonding of urethane or latex foam for upholstery and mattresses.

In terms of adhesives:

- PVA emulsions are the most common low cost adhesives used by wood workers and the furniture industry for bonding joints or enhancing the strength of nailed or screwed assemblies. They are sold as liquid products containing 50-60% solids and set rapidly at room temperature to give high strength bonds. However their moisture resistance is poor and loaded joints tend to creep, particularly at elevated temperatures. Moisture resistance can be improved by copolymerising with acrylic monomers or adding catalysts to cause crosslinking, but at increased costs.
- Thermoplastic hot melts such as EVA are not used in structural applications where high strength is required, but are commonly used in the furniture industry to attach decorative materials such as edgebanding to panels and table tops, and for wrapping of profiles. They are low cost adhesives whose application can be readily automated – edgebanding, for example, is done on automatic machines. Higher cost hot melts such as polyamides or RHMUs can be used where high performance or better heat resistance is required.
- Polychloroprene contact cements, both solvent-based and emulsions, are used for laminating countertops. The elastomeric nature of these adhesives makes them very effective in providing strong bonds to highly stressed joints. The solvent-based versions were also commonly used

for foam bonding but have been replaced by latex and sprayable hot melts because of solvent emission regulations.

### **7.5.6 Graphic Arts and Books**

Bookbinding is an important application area for adhesives and requirements are becoming more demanding. With many publishers planning for worldwide distribution, and given today's competitive market, bookbinding adhesives have to be very versatile. Software publishers, for instance, have to pay particular attention to end-use, since their manuals can end up anywhere in the world. They must be able to stand up in a wide range of climates and user habits.

Even domestic publishers have to be knowledgeable about binding methods and durability. Books not only must catch a buyer's eye when on the shelf, but also they must be able to withstand a lot of abuse. Adding factors such as cost competitiveness and turnaround time, there are many factors to consider when selecting an adhesive for a project.

Most books that are not stitched or stapled are made by the so-called perfect binding process using hot melt or emulsion adhesives. Perfect binding is a relatively simple process. The perfect binding machine collates the pages that make up the text of the book, then clamps the text just above the spine. The collated text passes over a saw that cuts off about 3 mm from the spine of each page. This ensures that each page will contact the adhesive, which is applied next.

Adhesive is applied to the entire spine of the book, and also about 3 mm up the front and back. This 'side adhesive' helps keep the cover closed and hides the roughened binding edge of the pages from view.

While the adhesive is still hot, a heavy paper cover is fed from a hopper and aligned with the text. As the cover feeds it is scored for both the spine folds/corners and the hinges. The hinge score is used in conjunction with the side glue to allow the cover to open freely. The cover is aligned exactly with the text and pressed onto the adhesive, which begins to harden immediately; within a few minutes books are ready to trim on three sides and ship.

When economy is foremost, perfect binding is a simple and inexpensive way to bind books.

Book binding adhesives fall into four main categories:

- Polyvinyl acetate (PVA) emulsions
- Ethylene-vinyl acetate (EVA) hot melts
- Rubber based hot melts
- Reactive hot melt urethanes

EVA hot melts are the most traditional method of binding. They are relatively inexpensive, cure quickly and form a good strong bond under most conditions. They tend to stiffen when cooled and, thus, do not hold up well under temperature extremes. It is difficult to use hot melts on heavily coated stocks or very heavy paper stocks.

PVA emulsions are applied cold. When they dry, the resins penetrate deep into the structure of the paper stock, forming a solid bond. PVA glues cure to a semi-soft state, providing a more flexible backbone than hot melts and performing better at low temperatures. Recently, ethylene-vinyl acetate emulsions have entered the market to give a soft polymer which creates a flexible film that is ideal for adhesion to low energy substrates, such as PVC, foils, coated paper and boards. They also give much better low temperature properties than hot melts.

Reactive hot melt urethanes (RHMUs) that give instant fixture and then cure to give crosslinked adhesives are considered to be the most flexible and durable bookbinding adhesives for

bookbinding. They yield products that lie flatter and require less backbone preparation than other adhesives. On the flip side, they are more expensive than other methods and the full curing time is between 24 and 48 hours, a definite disadvantage if costs or productivity are a issues.

A recent development in adhesives is to apply two hot melts, one after the other. The first hot melt is specially optimised for adhesion, and its purpose is to wet and bond the paper edges so that the book or catalogue has good durability. The second hot melt mates the cover to the pages and is responsible for the high production speed. Slower setting hot melts are used for the former, and faster setting ones for the latter since the bonding of the cover is far less difficult than the bonding of the paper edges. Both of the hot melt adhesives used in this system have to be coordinated to guarantee the desired high production speeds as well as the desired usability properties of the final graphic article.

So called ‘tipping-in’ adhesives are used for the attachment of permanent or removable supplements, credit cards or phone cards in direct mail packages or directly into newspapers and magazines. These adhesives allow the removal of items by the customer with no residual adhesive.

Other removable glues have a wide range of applications. A few spots or a continuous line of adhesive can be used in place of sticky-backed wafers to seal brochures or direct mailers; the adhesive can also be applied in a pattern, such as a circle or square. Hot melts or water-based adhesives can be used, with hot melts becoming very popular for high speed operations.

The traditional lick-and-stick adhesive, known as remoistenable adhesive in the binding and finishing world, has almost disappeared from stamps but remains a perennial favourite in the printing community, especially for those who work with direct mail. These adhesives are extruded hot melts or are applied in liquid form and then heat dried to remove the moisture. The adhesive is then reactivated by wetting it.

Remoistenable glues have limited applications but are commonly found on the flaps of reply envelopes and on the backs of promotional literature. There are two basic ways to apply remoistenable adhesives. Traditionally, cold, water soluble adhesive was transferred to paper via a wheel or a blanket. This process is beneficial because heat by itself does not activate the adhesive, making the final product laser compatible.

Hot melt extrusion is another way to apply remoistenable adhesives. Hot melts can be applied much more precisely than water-based systems and give a very polished and professional look with no curling of paper. Conversely, water-based adhesives often look dull, have rough edges, and tend to curl the paper because moisture is added to only one side of the sheet. In the US remoistenable adhesives must be approved by the FDA.

Resealable adhesives are temporary pressure sensitive adhesives with some tack but can be opened and closed repeatedly and leave no residue. One of the most common examples of a resealable adhesive is the 3M Post-It® note.

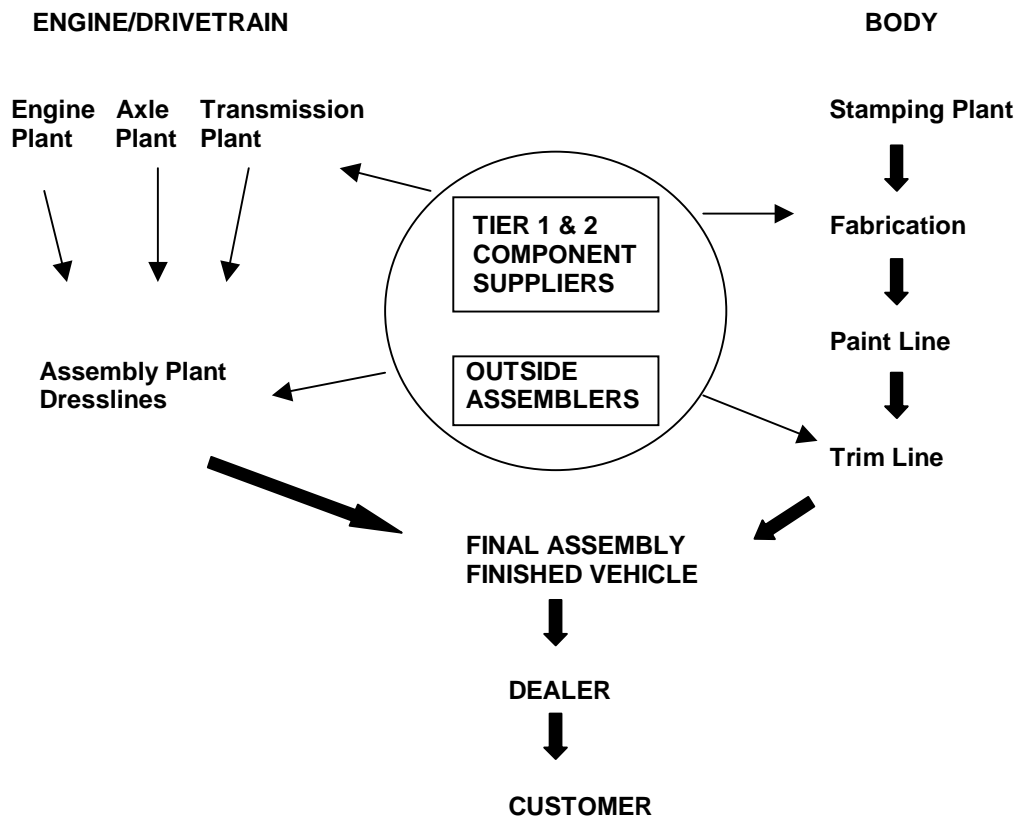
Other newer formulas allow items to have removable and repositionable qualities. This type of adhesive is often found on grocery store items where coupons are removed for immediate use. The level of peel strength and tack or residue can be adjusted depending on the formula used.

Other adhesives used in the graphic arts industry include cohesive (or self-seal) adhesives and pressure seals. Cohesives usually form a fairly strong bond and can only stick to themselves. Common examples would be the wraps found around packs of currency or restaurant napkins containing utensils. These can be formulated to form a permanent bond where the item is destroyed after one opening or can have several reclosures before they are thrown away. Pressure seals are special seals often used in direct mail pieces that require extremely high pressure to form the bond.

## 7.6 Transportation

The use of adhesives and sealants in the transportation industry is widespread and they are used at all stages of production of components, final assembly and after the vehicles are sold.

The essential components of a vehicle are the body, powertrain components (engine, axle, transmission), fuel system, cooling system, electrical system, brake system, interior and exterior trim. Although, the OEM auto manufacturers still control most of the powertrain and body components, many subassemblies like electrical and fuel systems, brakes and radiators are supplied by Tier 1 and Tier 2 component suppliers. There are opportunities at all points in the automotive value chain to use adhesives and sealants (Figure 7.4).



**Figure 7.4 Opportunities for adhesives and sealants in the automotive value chain**

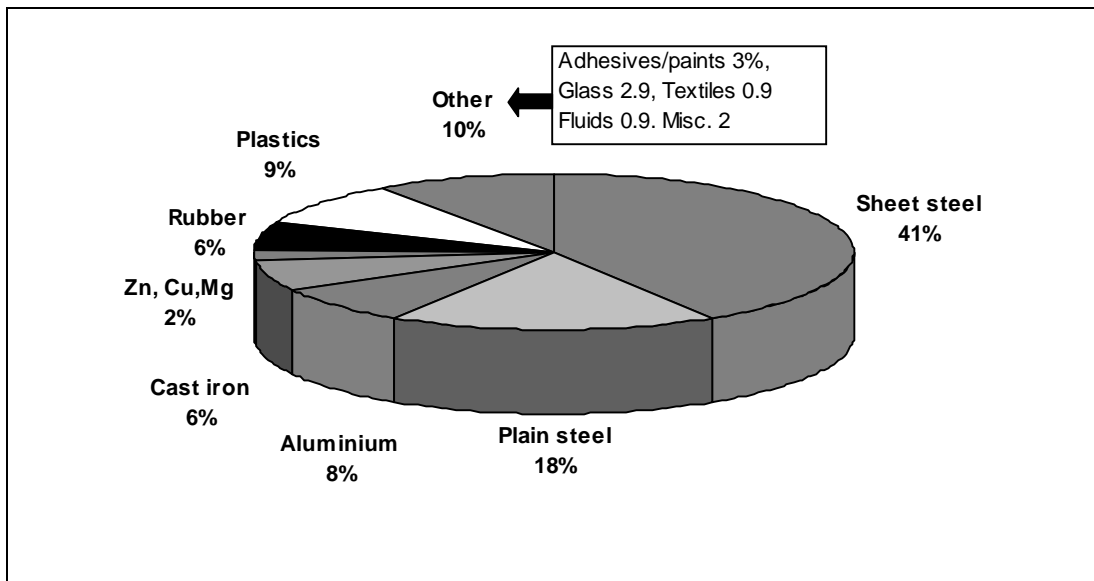
The OEM automotive business is directed at marketing adhesives and sealants through the final assembly of the vehicle, whereas the automotive aftermarket sells products to dealers, professional repair shops and for DIY.

### 7.6.1 OEM Automotive

The number of applications for adhesives in automotive has increased significantly in recent years with a continuous upgrading of systems to meet new requirements such as thinner steel panels, use of light metals such as aluminium and magnesium, more use of plastics, and higher operating temperatures and new fluids.



Figure 7.5 shows the different types of materials used in a typical car.



**Figure 7.5 Materials used in a typical car (% by weight)**

(Source: data from European Plastics Converters)

Typical automotive applications for adhesives and sealants are shown in Table 7.6.

Table 7.6 Typical automotive applications for adhesives and sealants		
Area	Typical applications	Typical products used
Powertrain	Threadlocking	Anaerobics
	Oil pan gasketing	Silicones
	Rocker cover gasket	Silicones
	Oil filter assembly	Plastisols, cyanoacrylates
	Clutch facings	Phenolics
Body	Hem flange bonding	Plastisols, epoxies, PU
	Body-in-white sealing	Plastisols, rubbers, PVC
	Roof bow joints	Rubber
	Anti-flutter stiffeners	SBR, polybutadiene
	Plastic panel bonds	Epoxies, PU
	Bumper bonding	Reactive acrylics, PU
	Cavity sealants	Expandable PU
Trim	Labels, decals	Acrylic pressure sensitives
	Rear parcel shelves	Hot melts, RHMU
	Sun visors	Hot melts
	Mirrors	Silicones
	Upholstered seats	Hot melts, RHMU
	Floor insulation	Hot melts
	Headliner	Hot melts, RHMU
	Dashboard	PU, hot melts
	Carpet bonding	Hot melts, pressure sensitives
	Windshield bonding	PU
Electrical systems	Headlight units	Epoxies, UV acrylics
	Rearlight units	Silicones, hot melts
	Spark plug seals	Silicones
	Motor bonding	Anaerobics, reactive acrylics, UV acrylics
Brakes	Disk pad bonding	Phenolics

### 7.6.1.1 Powertrain Applications

Numerous applications exist for anaerobic threadlockers and sealants in engines, transmissions and axles to create vibration-proof fasteners and seal fluid joints.

An important application for sealants is in formed-in-place gasketing where a liquid gasket is applied to flanges, which are then assembled and the liquid cures in place. The functioning of a formed-in-place gasket system is very different from that of a cut or moulded gasket. A conventional cut gasket creates a seal by compression, induced by the tightening of the fasteners. It is essentially a compressed spring, comprising flanges, gasket and fasteners. Any loss of tension in the system caused by stretching of the fasteners, vibration loosening, or creep or relaxation of the gasket will ultimately lead to failure. In contrast, a formed-in-place gasket does not cure until after assembly. It has metal-to-metal contact between the flanges, which, with the fasteners, carry all of the tension. Even if some tension is lost, the adhesion of the sealant will often prevent the failure of the system. It is very important that flange systems be specifically designed for or modified for formed-in-place-gaskets.

Two types of gasket sealants are commonly used, anaerobics and medium-modulus RTV silicones. Anaerobics require rigid flanges and small gaps, and cure to a rigid system that is designed to prevent any joint movement. They are not recommended for gasketing of plastic parts. Medium modulus RTV silicones can be used on rigid flanges, but are also useful in flexible flange situations in which joint movement is expected. In this case, it is very important that the flange design allows a sufficient gap, primarily to permit atmospheric moisture to cure the silicone and secondarily to maximise the joint movement capability of the sealant. RTV silicones have been used in the US since 1971 for formed-in-place automotive gasketing in engine, transmission and rear axle sealing. The weaknesses of early formulations, including poor oil resistance, poor adhesion, corrosion and lack of flexibility, have been overcome.

RTV silicones face strong competition from moulded silicone gaskets used by US manufacturers and European manufacturers have preferred to use moulded rubber gaskets in most applications. Furthermore, many applications are developing for liquid injection moulded gaskets that can be injected and cured into preformed grooves in an assembled component. Up until now, this has only been possible with silicones, but Freudenberg NOK G.P. has announced a family of non-silicone liquid elastomers:

- Nitrile
- EPDM
- Isoprene
- Fluoroelastomer

These materials promise to extend the range of elastomer performance available to liquid injection moulders. A related development is seal-in-place technology for fuel cells. Developed by Dow Corning in conjunction with fuel cell manufacturer Hydrogenics Corp., it is a cost-effective, automated sealing process that injects silicone materials into an assembled but unsealed fuel cell stack. The process substantially reduces stack assembly time and labour costs by eliminating the need to seal each cell in the stack individually. Typical fuel cells use as many as 1200 mostly static seals.

Recently, two companies have introduced UV cured sealants that can replace preformed rubber gaskets. Henkel-Loctite have a range of silicone-based products they call FastGasket® that can be UV or heat cured, whilst Dymax introduced a similar range based on urethane-acrylic and rubber-acrylic chemistry. These materials allow users to apply a liquid bead of sealant to a part and then cure it in place with good adhesion to the surface of the part. Customers can then use the pre-gasketed part when required or can ship the part to their customers. This type of system gives tremendous flexibility to a customer to make a wide range of cure-in-place gaskets using

programmable robotic applicators, without the costs of creating a new mould for every new gasket. However, capital costs are high, creating an entry barrier for small users. Another limitation is creating UV systems that can meet the performance requirements of some industries which are accustomed to using high performance elastomers such as acrylic rubber (ACMs), hydrogenated nitrile (HNBRs) and fluorinated elastomers (FKMs). It is perhaps significant that patents are starting to appear on UV curable versions of these rubbers [1].

It seems likely that liquid form-in-place gasketing will decline because of major changes in legislation and the performance requirements of the OEMs.

Among the major drivers of demand for higher performance gaskets and sealants in automotive applications have been:

- technological developments
- OEM specifications
- warranties
- legislation

Technologies, such as the introduction of fuel injection systems, new aggressive fuel additives, higher engine compartment temperatures and so on have resulted in upgrading to higher performance materials.

In tandem OEM specifications have been developing, in general, towards imposing higher performance requirements. The result has been a trend to upgrade the materials used in component manufacture. Illustrative of this trend are the general temperature and permeation resistance requirements imposed by the OEMs.

Warranties are lengthening and broadening in coverage. This has also been a driver of upgrade to higher performance sealants.

Legislation has also imposed increased demands on the elastomers used for automobile sealants. Most notable has been environmental legislation to reduce primary pollutants. The US SHED and European Euro 2000 legislative projects, which call for dramatic reductions in fugitive emissions, are two examples of this.

Meeting these regulations calls for higher fuel permeation resistance resulting in progressive upgrading to lower permeation elastomers.

At the same time there have been changes in automobile design that have modified the performance requirements. For example, cleaner but higher temperature engines have shifted the priorities from chemical resistance to heat resistance.

Among the specific challenges for the automotive seals and gasket industry are:

- New durability and warranty demands from the OEMs where 200,000 miles may be expected with 150,000 being the norm.
- The continuous goal to improve fuel economy is leading to the use of lower viscosity lubricants with aggressive anti-friction additives.
- Increasing exhaust emission requirements in cars and trucks, necessitating new oil additives.
- Hydrocarbon emission requirements, for example, low emission vehicle standards, such as LEV-2.
- Demands for OEMs to extend oil and antifreeze change intervals.
- New fuels for cars and trucks.
- Increasingly demanding tests for low temperature start-up.

Most sealant materials are polar materials and withstand non-polar materials like hydrocarbon based fuels and lubricants quite well. However, several of the upcoming changes in fuels and lubricants will create serious challenges for the industry. These changes can be summarised:

- Lower viscosity oils – in general low viscosity fluids find leak paths easier than thick ones and problems are expected particularly in cold-start situations, where the dynamic response of a cold rigid elastomer seal is normally much slower than the thinning of the oil with increasing temperature.
- Aggressive oil additives – additives will be used at higher concentrations and will be more basic to counteract the acid build up in oils caused by new Exhaust Gas Recirculation engines (EGR) and longer drain intervals. These amine type additives can plasticise and cause swelling of some elastomers, but can also crosslink any residual unsaturation in hydrocarbon elastomers, leading to hardening.
- Oxygenated fuels – the highly polar ethanol, which will become increasingly prevalent in fuels, will contaminate oils during cold-crankcase starts and will cause serious problems for seal makers. Gasoline/ethanol blends have much higher permeation rates through elastomers than straight gasoline. Even the vinylidene fluoride groups in fluoroelastomers are sites for permeation, although higher levels of tetrafluoroethylene can mitigate this, at the expense of sealant flexibility. Only PTFE seems to resist permeation completely.

Although the use of RTVsilicones is expected to decline in fluid sealing applications, large growth is projected for sealing and weatherproofing of electronic components.

#### *7.6.1.2 Body Applications*

The traditional unibody construction method consists of stamped steel body panels, spot welded together (often described as ‘body-in-white’) to which stamped steel fenders, doors, hood, and deck lid are bolted.

Both sealants and adhesives are used widely in automotive applications. One of the advantages of an automotive production line is the fact that the high temperature paint bake ovens (160-205 °C) can be used to cure the adhesives and sealants.

Sealants are used for all the joints. In the automotive body context a sealant is any organic material used to prevent air, dust, water or noise from entering the vehicle and to prevent corrosion of the joints.

Sealants come in a variety of forms, including:

- bulk pumpable liquids
- Sprayable liquids
- semi-solid pastes and putties
- extruded
- die-cut parts

Important properties of sealants include good adhesion to steel, flexibility to withstand constant motion in a vehicle and good environmental resistance, including heat and cold, road salt, etc.

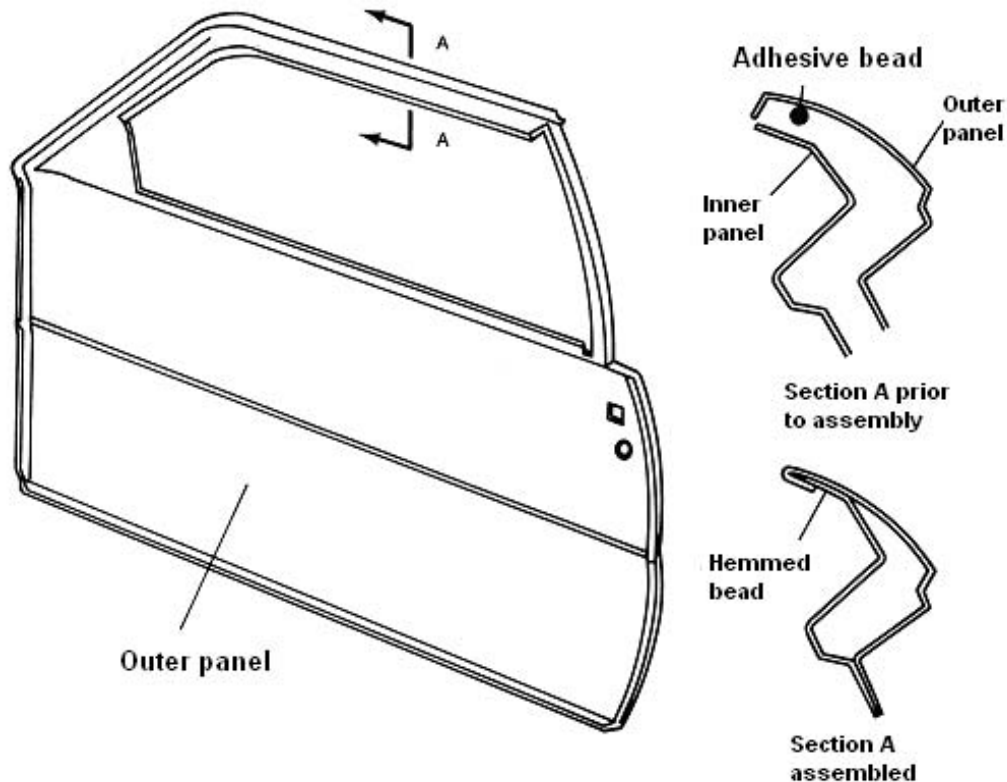
A number of technologies are used for body-in-white joint sealing and underbody seals. These include vinyl plastisols, sprayable PVC, butyl rubber and polypropylene oxide.

Antiflutter adhesives are used to adhere and isolate outer body panels (i.e., hoods, doors and decklids) from inner reinforcements. They need to be able to adhere to steel contaminated with stamping lubricants and be resistant to wash-out from phosphate cleaning systems. Many of these

adhesives are designed to expand during the paint-bake process. Heat curable rubber formulations are used commonly including SBR and polybutadiene.

A modern trend is to use adhesive sealants to carry out the dual function of bonding and sealing. Traditionally the inner and outer panels of doors, trunk lids and hoods use hemmed flanges sealed with vinyl plastisols and the joints reinforced with spot welds. This led to a requirement that sealants had a weld-through capability. By using a high strength epoxy adhesive, the welds can be eliminated, thus giving a smoother finish.

Figure 7.6 shows a typical construction for attaching the panels of a door.



**Figure 7.6 Hem flange bonding on car door**

Both one-part and two-part epoxies have been used. In the case of the one-part adhesive, induction heating is used to give enough handling strength to the assembly prior to completing the cure in the paint-bake oven.

Two-part epoxies have performance advantages over one-part systems in providing rapid development of handling strength for hem-flange assemblies. They can avoid the use of spot welding in many assemblies. However, more complicated handling and application equipment, plus the necessity of ensuring accurate measuring and mixing of the adhesive and hardener have hindered their use. Ford and 3M have recently developed a novel method of controlling the mix ratio by measuring it continuously using a tagging system that incorporates microscopic stainless steel-coated glass bubbles in one-component of the adhesive. These can then be detected by two eddy current sensors integrated into the dispensing equipment. The technique enables 100% knowledge and 100% control of the dispensing ratio.

The emphasis on developing lightweight car bodies can be achieved in steel by reducing the panel thicknesses used or by using specifically lighter materials such as aluminium, magnesium or fibre-reinforced resins.

The mass production of cars with aluminum and plastics replacing steel in body structures is still some years away for both cost and performance reasons, but many components such as doors, fenders, hoods and trunk lids are now manufactured out of materials like thermoset polyurethane, unsaturated polyester and aluminum. Mechanical fastening and heat curing cannot be used with these systems and adhesive bonding with two-component epoxies and polyurethanes is employed.

H. Flegel of Daimler-Chrysler has described the use of structural adhesives in body construction and concluded that modern lightweight design, safety and modular concepts can no longer do without adhesively bonded joints and the strength they provide in a crash scenario [2]. With reference to the Mercedes S-Class coupe, he describes that it is a multimaterial design using steel in areas such as roof pillars, longitudinal members and cross members that are subjected to high loads during a crash; aluminium for the manufacture of large-area parts such as the hood, roof, tailboard and rear fender; magnesium for the interiors of the doors and plastic for attachments such as the trunk lid, bumper and front fender.

The body-in-white is adhesively bonded and reinforced using self-piercing rivets. The combined joining method considerably increases the energy absorption capacity and hence the crash resistance, in contrast to spot-welded joints. In addition the structural rigidity of the body can be increased, depending on the vehicle design, by about 15 to 30% compared with welded components. Some 90 metres of adhesively bonded joints are used in this vehicle.

Aston Martin have developed applications for their Vantage car that use an epoxy bonded aluminium frame to which aluminium and composite panels are bonded using flexible urethane adhesives.

The use of filled thermosets and thermoplastics in panels is expected to increase significantly over the next few years. Automakers will replace traditional steel components with more reinforced thermoset composite plastics in 2002, according to the US Automotive Composites Alliance (ACA), an industry trade group that tracks the growth of composites annually. The use of reinforced thermoset composites has nearly doubled in the last decade, and is expected to increase 47% during the next five years. Over 86% of all automotive composites are SMC or BMC and the ACA industry projects OEMs will use 192,000 tons of reinforced thermoset composites in 2002 and 234,000 tons by 2004. In Europe, use of unsaturated polyesters in vehicles is expected to be flat over the next 5 years, primarily because of competition from reinforced thermoplastics, which are considered to be easier to recycle.

#### *7.6.1.3 Electrical Applications*

Headlight applications include bonding glass and plastic lenses to reflectors, sealing exhaust holes, bonding and potting halogen lamps. In fact, glass headlight lenses on automobiles have been virtually replaced by transparent polycarbonate plastics. Epoxies and UV acrylics are the major adhesives used in headlight applications. Tail lights, turn signals, cornering lamps, back-up lights, and fog lights are all made of polycarbonate plastics or, in some cases, acrylic plastics. Silicones and hot melts are used in sealing plastic tail-lights and interior lamps. The use of more plastics in these assemblies will encourage the use of more adhesive bonding. For example, some 23 million headlight reflectors are currently manufactured globally from unsaturated polyester bulk moulding compound.

#### 7.6.1.4 Trim Applications

The new steel panels used in vehicles are not as heavy as in older cars, but being thinner are not as strong. The use of polyurethane windshield adhesive/sealants to replace the traditional butyl sealants has enabled the windshield to become a structural part of the vehicle as it supports the roof. OEM adhesives are typically one-component moisture cured urethanes that take several hours to cure and give bonds with tensile shear strengths of 5 to 8 MPa (700 to 1100 psi). The products are pigmented black to give resistance to UV. Aftermarket adhesives often use two-part urethanes to speed up the repair process.

10 years ago, thermoset polyurethanes were the mainstay of bumper manufacture (about 80%). Now the majority of modern plastic bumper system fascias are made of thermoplastic olefins (TPOs), polycarbonates, polyesters, polypropylene, polyurethanes, polyamides, or blends of these and reinforced with glass fibres, for strength and structural rigidity.

Two-part polyurethanes and reactive acrylic adhesives have been used widely for bonding the fascias to the reinforcement beams.

Mirrors are sealed into their housings with RTV silicones. Electrochromic (self-darkening) mirrors need specially formulated epoxy adhesive-sealants to prevent diffusion of moisture and air into the electrochemical cells inside the mirrors.

Internal trim applications for adhesives include:

- Bonding of seat fabrics to foam
- Bonding carpets to PP, ABS, polycarbonate, RIM urethane
- Bonding door panel trim, e.g., TPO or fabrics to steel.
- Bonding package trays, e.g., PU foam to woodmat
- Bonding wire harnesses to headliners
- Bonding headliners, e.g., fibreglass composite to foam and fabric
- Bonding labels and decals

Adhesives for most of these applications are not of the structural load-bearing type and their choice is often dictated by ease of handling and assembly.

Historically, solvent-based contact adhesives, such as polychloroprene were used, but have been phased out for environmental reasons.

A number of adhesives are used including latex systems, reactive acrylics, water-based and two-part urethanes, and hot melts. Prompted by more demanding specifications used by Japanese manufacturers and longer warranties, US and European OEMs have increased their requirements for interior adhesives with emphasis on higher temperature resistance, up to 100 °C in many cases. This has created opportunities for technologies like reactive hot melt polyurethanes that can give instant fixturing and then crosslink with atmospheric moisture. However, improvements in these adhesives are still needed, particularly in the rapid development of green strength to allow earlier handling of parts.

Pressure sensitive adhesives (PSAs) are widely used to attach labels and decals and are increasingly being used for trim bonding, particularly in the form of two-sided tapes or transfer tapes. New PSAs show good adhesion to polyolefin based substrates.

In internal trim, many hard trim applications are moving from plastics like ABS toward thermoplastic polyolefin (TPO) as the material of choice for both performance and cost reasons. In addition to penetrating the hard trim components, TPO is also moving into instrument panel skins

replacing vinyl, and into air bag covers replacing urethane and thermoplastic polyester. Bonding of TPO creates new challenges for adhesives manufacturers.

Major adhesives and sealants suppliers to the OEM auto industry include Henkel-Terason, Henkel-Loctite, Ashland Chemical, Dow Automotive, Gurit Essex, 3M, Uniseal, Vantico, Kommerling, Bostik Findley, Lord Corporation, ITW-Plexus and Permabond.

### **7.6.2 Automotive Aftermarket**

The automotive aftermarket is defined as any service, maintenance, parts, and equipment purchased for a vehicle after it leaves the showroom. It includes both the professional and DIY maintenance and repair segments. Products are distributed in several ways including auto dealers, speciality automotive distributors and retail outlets.

A wide range of adhesives and sealant products are sold into this market and several companies use the term 'OEM approved product' to get market acceptance.

RTV silicones and anaerobics are very versatile products for form-in-place gasketing, allowing mechanics to make a wide range of gaskets and avoid stocking a lot of moulded gaskets.

For over 90 years, cut and moulded gaskets have been treated with dressings to aid in sealing. Gasket dressings, such as mineral-filled mixtures of wood rosins, serve to hold gaskets in place on flanges during assembly and shipping; fill in substrate imperfections; and, through adhesion, assist in maintaining a seal under joint movement. These gasket dressings are used widely in the aftermarket under such brand names as Hermatite in Europe and Permatex in the US.

Two-component versions of polyurethane windshield adhesives are used to replace damaged windshields, whilst primer-cured anaerobics are used to bond rear view mirrors to the inside of windshields.

Anaerobic threadlockers are an invaluable aid to mechanics in re-assembling threaded parts. Filled reactive acrylics can be used to repair damaged threads.

UV acrylics are used to repair cracks and 'bullseyes' in windshields.

Polychloroprene based sealants are widely used as versatile weatherstripping sealants and general purpose interior trim adhesives.

Filled epoxies are used to repair holes in fuel tanks and radiators.

Silicate-based sealants and tapes are used to repair leaking exhaust systems.

The largest single product in the aftermarket is for body-fillers, used to repair exterior body panels. Most of these are based on highly-filled unsaturated polyesters. According to the Composites Fabricators Association some 23,000 tons of body fillers was consumed in the US in 2001, although this is probably the least profitable product in the aftermarket.

Important suppliers to the aftermarket in the US are 3M, Permatex, Bondo (division of RPM), Fiberglass Evercoat (division of ITW) and Dow Automotive. In Europe, Holt Lloyd, Hylomar, Hammerite, Henkel-Terason and Dow Automotive are leading suppliers.

### **7.6.3 Aerospace**

Controlled adhesive bonding of aluminium aircraft structures began in the 1970s with the Primarily Adhesive Bonded Structure Technology (PABST) funded by the US Air Force. This programme



determined the best surface treatment procedures, optimum joint designs, and application and storage procedures for adhesives with a goal of producing repeatable and reliable bonding.

Table 7.7 shows the main types of adhesives used in aircraft construction.

<b>Table 7.7 Adhesives used in aircraft construction</b>	
<b>Type</b>	<b>Major application areas</b>
Epoxy	Bonding metal honeycombs and skins
Nitrile phenolic	Bonding metal honeycombs and skins for high temperature situations
Acrylic	Bonding interior plastics
Silicone	Bonding and sealing interior plastics
Polyurethane	Bonding plastics and composites
PSAs	Bonding interior plastics

Adhesives are used as two-component liquids and pastes, one-component heat cured liquids and pastes (often two-component systems that have been pre-mixed and frozen for storage), films and pressure sensitives. Because of the emphasis on light weight in aircraft many adhesives are supplied as syntactics – these are essentially foam type materials containing spherical hollow glass spheres.

Panels for both exterior and interior use are fabricated from aluminium in a sandwich type structure using a honeycomb core with panel skins. This gives a combination of very high strength and low weight. Either aluminum or materials like aramid can be used to construct the honeycomb cores.

Heat-curable epoxy paste and film adhesives are used to bond the honeycomb and to bond skins to honeycombs. Nitrile phenolics are often used for high temperature applications above 240 °C where they show better strength retention than epoxies. The adhesives are cured in heated presses.

Completed panels are often bonded together using simple tongue and groove-type joints.

Epoxy graphite plies are commonly used to form laminate structures such as in aileron (surface at the trailing edge of the wing) construction.

Although adhesives and sealants are used in bonding and sealing of critical aircraft structures such as fuselage and fuel tanks, the highest volume of products are used in interior applications such as bonding panels, seats, tray tables, sealing overhead bins, galleys and toilets, etc. There is a large repair industry for many of these components. The adhesives are required to be self-extinguishing and exhibit the low flame, smoke and toxicity characteristics required to comply with regulations governing materials used in aircraft interiors.

Sealants are applied throughout the aircraft primarily to seal out moisture and contaminants. This helps prevent corrosion, particularly on faying (i.e., closely or tightly fitting) surfaces, inside holes and slots, and around installed fasteners. Sealants are also used to seal fuel tanks and pressurised components. They are applied using tubes, spatulas, brushes, rollers, or spray guns. Sealants are often stored frozen and thawed before use, and many are two-component systems that cure after mixing.

Sealants are also used widely in aircraft to maintain pressurisation in cabin areas, to retain fuel in storage areas, to achieve exterior surface aerodynamic smoothness, and to weather-proof the airframe. They need to have special properties for aerospace applications, including:

- High and low temperature resistance (–60 to 120 °C)
- Resistance to jet fuel
- Adhesion to aluminum, stainless steel, titanium and composites
- Ability to maintain electrical continuity

Two-part polysulfides with MnO<sub>2</sub> catalysts are the most widely used products because of their outstanding fuel resistance and flexibility.

Dichromate-cured polysulfides are used for applications where increased corrosion resistance is required. Epoxy cured polythioethers are used for faster curing. Non-curing polysulfide pastes are often used as channel sealants round fuel tanks. Fluorosilicones and cyanosilicones have also been used for this application.

Typical applications for sealants are:

- Sealing fasteners on fuel tanks
- Fillet and channel sealing on fuel tanks
- Windshield and canopy sealants
- Firewall sealants
- Access door gaskets
- Floorboard sealants
- Potting and sealing electrical connections and cables

Aerospace sealants are expensive - for example a general purpose polysulfide for fuel tank sealing costs \$50-60/kilo in a small package.

Major companies supplying to the aerospace industry are the PPG Aerospace division (PPG-DeSoto), Akzo Nobel, Henkel-Loctite, 3M, Vantico, Sia and Chemetall.

#### **7.6.4 Marine**

The marine market segment includes all composite materials used for pleasure boats, personal watercraft, naval boats and ships, racing craft, as well as commercial ships and component parts, equipment, motor covers, moorings, marina docks and floats.

The marine industry provides good opportunities for the use of adhesives. The top 5 countries in terms of total annual boat shipments in the world are the US, France, UK, Italy and Germany. Boats made of composite materials dominate the boating industry. Fibreglass boat manufacturers use a variety of raw materials such as glass roving, woven fabrics, mats, SMC, vinyl ester resins, polyester resins, epoxy, balsa core, teak, foam, honeycomb cores, gel coats, for production of boat hulls, decks, bulk heads, cock-pit, hatches, lids, interiors and more.

Phenolic resins are used to manufacture the most durable of plywood, called marine plywood and are used in repair operations.

Epoxy adhesives are widely used to make laminate structures of marine plywood and plywood/polyester.

Mixable reactive acrylic adhesives have become very important in bonding fibreglass in this industry because of their high performance and the ability to have a controlled induction time, allowing time to position parts before the adhesive cures.

Sealants for marine applications have to bond and seal a range of materials and have good water resistance. The most widely used materials are polysulfides, polyurethanes and silicones.

Two-part polysulfides are commonly used sealants in boats because of their excellent water resistance and good bonding to materials like teak in decking. Polysulfides are the best sealants for the seams in both laid and overlaid decks, due to their resistance to fuels and solvents in general, and to teak cleaners in particular. They are not usually recommended for bonding thermoplastics. Marine grade polyurethanes and silicones will bond well to a wide range of surfaces including

many plastics. Both polyurethanes and silicones have good flexibility, which is important in a boat application. The essential difference between them is that the polyurethane will have much higher adhesive strength, which is usually an advantage, but can be a problem if parts need to be disassembled. Clear UV resistant sealants are often specified for applications like bonding acrylic windows. Silicones are very versatile sealants in boats but are not normally recommended for below the waterline applications.

## **7.7 Surgical Adhesives**

The use of adhesives in surgery goes back to the Vietnam war when MASH units were losing many patients who were suffering from grave wounds of the chest or abdomen, and who bled to death before surgery could be performed. A special surgical team experienced almost miraculous results by spraying cyanoacrylates on the wounds, stopping bleeding almost instantly, and allowing time to treat the wounds by conventional means. Thus a revolutionary advance in surgical procedures was demonstrated and many were saved who would have died. However, the development of these adhesives was frustrated for over 30 years in the US by the inability to get FDA approval, mainly on the grounds that foreign objects implanted in the body might cause cancer many years into the future.

The worldwide wound closure market is estimated at \$1.6 billion according to Medical Data International with \$800 million being for external wounds, \$300 million for Emergency Room lacerations and \$500 million for internal applications. Most of this business uses conventional techniques such as sutures, staple and tapes. The global market for tissue adhesives and sealants is currently around \$300 million, according to Warburg, Dillon and Read Inc.

There are three categories of adhesives and sealants used:

1. Surgical sealants are absorbable materials used primarily to control internal bleeding and to seal tissue
2. Biologically based surgical adhesives that are stronger than sealants, but typically non-absorbable
3. Synthetic surgical adhesives, specifically cyanoacrylates, which are strong adhesives and non-absorbable.

The internal wound market comprises:

- Sutures: the use of needle and thread
- Staples: the use of metallic devices to hold the tissue edges together
- Fibrin sealants: based on natural fibrinogen and thrombin
- Cyanoacrylates: outside of US only. Experimental in US.

Fibrin sealants and adhesives are natural substances used for stopping bleeding and sealing tissues in many surgical procedures. They are derived from human or animal blood products. They work in a manner similar to the natural clotting of fibrin. A solution of fibrinogen is mixed just before use with a thrombin solution containing calcium ions. The thrombin converts the fibrinogen into fibrin in the presence of calcium ions and the fibrin spontaneously polymerises to form a clot. The limitations of the technology are its two-component nature, its slow cure and low strength compared to mechanical methods or synthetic adhesives. Fibrin sealants have also been used as a carrier for other compounds – to slowly release antibiotics at the site of an infection, to deliver chemotherapeutic agents to tumour cells, and to deliver growth factor for healing of cartilage. Fibrin products are marketed by several companies including Thermogenesis Corporation, Cryolife and Baxter Medical.

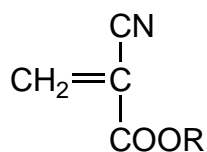
Cyanoacrylate adhesives have proved beneficial in the following medical procedures mainly outside the US:

- Sutureless surgery, particularly in rejoining veins, arteries or intestines
- Ophthalmic surgery, sealing punctures or lesions in the eyeball with sight-saving results
- Cosmetic surgery, replacing or supplementing sutures, with reduced scarring
- Bleeding ulcers can be sealed to protect the ulcer from stomach acids while healing proceeds
- Repairs of soft organs, lung lesions, etc., are easier than by conventional methods
- Dental surgery for sealing tooth sockets after extractions and in periodontal surgery where postoperative pain is greatly reduced.

### 7.7.1 Advances

In the late 1990s approval was finally received in the US for cyanoacrylates for external (or 'topical') applications. There were several developments that led to this approval:

- (1) New monomers – Most cyanoacrylate adhesives that are used in industry or sold at retail are based on methyl or ethyl cyanoacrylate.



#### 2-cyanoacrylate

where R = -CH<sub>3</sub> methyl  
 -CH<sub>2</sub>CH<sub>3</sub> ethyl

These monomers have been shown to be unsuitable as tissue adhesives, mainly because of tissue inflammation, tissue toxicity and poor flexibility. More suitable monomers are *n*-butyl cyanoacrylate or octyl cyanoacrylate. However, the higher analogues biodegrade at slower rates than the lower alkyl cyanoacrylates.

- (2) New purification and sterilisation procedures – The preparation of high purity monomers, often doubly or triply distilled, has been a key step in preparing medical grade adhesives. Also it has been shown that the adhesives can be sterilised by heat, gamma radiation or electron beams.
- (3) New stabilisers and plasticisers – The stabilisers used in industrial or consumer cyanoacrylates, typically strong acids and quinones have often caused tissue toxicity problems and special stabilisers have been developed. Also plasticisers, used to give enhanced flexibility to the cured adhesives have had to be carefully chosen.
- (4) Pioneering efforts – A major factor in gaining approval was the persistence of companies like Closure Medical (Raleigh NC) and its predecessor companies, Tri-Point Medical and BioNexus who have worked on this technology for over 15 years.

The external wound closure market consists of four distinct segments:

- Sutures: the use of needle and thread
- Staples: the use of metallic devices to hold the tissue edges together

- Adhesive strips: the use of small pieces of tape, often ‘butterfly’ shaped
- Cyanoacrylate adhesives: the gluing together of the edges of wound

Table 7.8 shows the relative benefits and weaknesses of the different methods.

<b>Table 7.8 Relative merits of wound closure methods</b>		
<b>Method</b>	<b>Benefits</b>	<b>Weaknesses</b>
Sutures	Long history High strength closures Lowest failure rate	Tissue damage due to needles Slow process Need to remove Anesthesia required High cost
Staples	Fast procedure No needle sticks Low cost	Not as strong as sutures May interfere with imaging techniques
Tapes	Fast procedure Painless No needle sticks Low cost Easy removal	Not as strong as sutures Adhesion problems – hair or moisture Highest failure rates
Adhesives	Fast procedure Painless No removal required Low cost	Not as strong as sutures Some failures due to lack of flexibility

The two leading cyanoacrylate adhesives are Dermabond (developed by Closure Medical and marketed by Ethicon) and Indermil (developed by Loctite and marketed by the USS/DG division of United States Surgical). Both of these products are FDA approved for topical applications. Other providers of medical-grade cyanoacrylate products targeting this market opportunity include GEM/Biovascular, B. Braun Melsungen, Medlogix Global, Chemence and GluStitch.

Henkel estimate the current annual global market for cyanoacrylate tissue adhesives at 2.5 million units, which extrapolates to a \$200 million market at selling prices of \$40 per unit.

A major disadvantage of cyanoacrylate adhesives is that one of the degradation products is formaldehyde, which is toxic to the surrounding tissues and this is one reason that cyanoacrylates have not found favor with the FDA for internal tissue closure. Recently, Chemence [3] have patented the use of copolymers of butyl 2-cyanoacrylate, glycolide, lactide, and  $\epsilon$ -caprolactone monomers. The adhesives from these copolymers are characterised by increased biodegradability, increased viscosity and increased flexibility with reduced generation of formaldehyde.

The use of medical adhesives as a barrier for the protection of skin is a relatively new concept. LiquiShield® from Medlogix is a topical, liquid barrier film that is painted onto the skin in a very thin layer in order to provide protection against skin damage caused by friction, shear and/or the presence of moisture which can lead to skin breakdown, particularly in radiation patients, amputees utilising prosthetic limbs, stoma patients, bedridden patients, paraplegics, quadriplegics and individuals with generally compromised skin integrity. Liquiderm™ is from Closure Medical and the company is seeking marketing clearance from the FDA for an over-the-counter liquid adhesive bandage that forms a barrier film intended to cover minor cuts and scrapes, minor burns, and other minor irritations of the skin and help protect them from infection. Closure Medical has also introduced Soothe-N-Seal™ canker sore relief that is the first cyanoacrylate medical device approved by the FDA for the over-the-counter consumer market. The adhesive has clinically demonstrated the ability to provide immediate and long-term pain relief associated with oral ulcers.

Other bio-adhesives have been identified over the years, including barnacle adhesives and mussel adhesives, where acidic proteins secreted by these species are crosslinked by enzymes to give strong adhesive bonds. However, production difficulties have hindered their development.

Australian researchers have reported on 'Frog Glue' a natural substance secreted by a species of frog in Australia and which appears to give high strength bonding in knee meniscal repair.

After many years of frustration, tissue adhesives are being taken seriously by both doctors and the FDA. We can expect approval of adhesives for internal wound management in the near future. Some analysts are predicting a multibillion industry developing over the next 10 years.

## **7.8 Plumbing**

Plumbing fittings comprise mainly high pressure threaded joints or low pressure plastic fittings.

Anaerobic sealants have gained wide acceptance for sealing metal threaded joints because of their ease of application and high performance.

Solvent based adhesives/sealants are still widely used for low pressure applications in the plumbing industry for bonding and sealing plastic pipe systems. Typical formulations of these so-called 'pipe dopes' use solutions of PVC, CPVC and ABS dissolved in solvents such as methyl ethyl ketone, cyclohexanone and acetone.

## **7.9 Gas Pipelines**

The supply of gas for home or industrial use has been practiced for some 200 years. Although coal or 'town' gas has been replaced by natural gas in most countries, many of the old town and city gas mains are still being used, many over 100 years old.

Natural gas is transported from the wells through high pressure transmission pipelines and then is passed through distribution pipelines at much lower pressures into homes and factories. Although many new systems use welded steel or plastic pipelines, many of the old distribution systems consist of old cast iron pipes. These pipes can leak for many reasons, including corrosion, earthquake damage and most commonly leaking joints. Cast iron pipe systems are short sections joined by large bell joints that have lead, rubber or jute sealants or packings. Although many of the pipes themselves are still in good condition, the joints have developed serious leak problems, particularly since dry natural gas has dried out some of the packings.

Technology was developed in the UK to seal the joints. One system developed by PLCS is a polyurethane system that completely encapsulates the joint and has been very successful. However, the most innovative and cost-effective system was developed by Chemence. The basis of the repair method is to inject a highly penetrating, anaerobic sealant into the space just behind the lead or rubber seal. The sealant is transported all around the joint face by capillary action and penetrates right into the leakage paths where it cures to a flexible polymer. Thus the sealant is applied to the most critical points - the leakage paths. Well-tried methods of application are available for most types of joints up to a metre in diameter for low and medium pressure systems up to 2 atmospheres.

The sealant and application method has been subjected to exhaustive testing and assessment in the USA and the UK and meets all the performance requirements of the gas industries in both countries. In the US, a programme of testing to meet US requirements was successfully completed at Cornell University. In the UK, testing was carried out to the British Gas performance specification in the early 1990s resulting in full approval for use throughout the UK.

In addition to proven performance, the real benefit of the Chemence system is that it minimises the amount of excavation required – the sealant need only be applied to one point in the joint and will

wick around the entire circumference of the pipe by capillary action. Encapsulation techniques require much larger excavations to expose the entire joint. Recently, sprayable versions of the anaerobic sealant have been developed which, when applied internally to joints can seal joints over several hundred feet of pipe from one excavation point. Chemence report that over 750,000 joint repairs have been carried out since the mid 1980s with success rates of over 95%. Cost savings in the range of 50% to 75% are made compared to conventional encapsulation repairs.

There is considerable opportunity for growth in this technology worldwide, e.g., in the USA, the gas industry operates approximately 90,000 km of cast iron gas pipe, with joints at 4 metre intervals, totaling some 30 million pipe joints. In the New York City metropolitan area alone, there are nearly 7,500 km of gas pipe line.

## **7.10 Porosity Sealing**

Most castings and powdered metal parts have porosity, inherent in the powder metal compacting and sintering process and caused by volatilisation of organic impurities in castings. With castings such as iron or aluminium, this porosity allows fluid leakage and with powdered metal parts, can cause severe plating problems. Pores can be quite large, designated as macroporosity, or very small, called microporosity.

Sealing of the pores is a routine necessity and is carried out by impregnation with a liquid sealant followed by a curing step.

The sealants that have been used are:

- Sodium silicates
- Unsaturated polyesters
- Acrylics

Water solutions of sodium silicate are the oldest types of impregnants and have the benefits of low cost and very high temperature resistance (over 300 °C). They suffer from long curing times and high shrinkage and are best suited for sealing macroporosity.

Unsaturated polyesters are polyesters diluted with styrene monomer and are fairly low cost impregnants of high viscosity, which must be cured at high temperatures for long times. Their high viscosities again makes them most suitable for sealing large pores.

The newest types of impregnants are based on acrylics, usually methacrylate monomers. They are low viscosity, high cost impregnants and have revolutionised porosity sealing because of their ability to penetrate microporosity and cure very quickly. The earliest versions were pioneered by Loctite Corporation (USA and Europe) in the 1970s and were based on anaerobic resins. Processing typically involved placing parts in a basket, immersing in the resin and removing air from the system and the pores by pulling a vacuum. On release of the vacuum, the impregnant flowed into the pores. The next step in the operation was to raise the basket and spin the basket of parts (called 'centrifuging') to remove excess resin and re-use this resin. Because anaerobic resins are very expensive compared to sodium silicates and polyesters, this was a step that was critical to the economic viability of the process. Following the centrifuging, parts were rinsed in a chlorinated solvent bath and then placed in an activator bath, again based on chlorinated solvents. This process was carried out entirely at room temperature avoiding the heating of parts which can lead to bleed out of resin from the pores. Developments in the 1980s led to the use of aqueous detergent washing and activating solutions. Several process variations are possible with all types of impregnants, sometimes involving dry vacuum, wet vacuum and pressure cycles to seal very difficult parts.

Whereas the anaerobic process was initially very attractive to new installations in relatively high tech companies, it proved difficult to convert long time users of silicates or polyesters, because of

the capital costs of building a rather sophisticated system for anaerobic impregnants. Ultraseal International (UK) and other companies overcame this hurdle by making a heat cure version of the methacrylate resins, which could be cured in less than 30 minutes at 90 °C. This allowed customers put this new resin into their old polyester plants, cure the parts in hot water and get better performance with a much cleaner and easier to handle system.

In the 1980s, the methacrylate resins started to make inroads into new sealing areas, particularly in the sealing of electrical and electronic components.

Two major improvements in processing in the last few years have helped to lower the overall cost of acrylic impregnation. The first improvement involved incorporating emulsifying agents and hydrophilic monomers into the systems which allowed rinsing of parts in plain water, and second, by careful choice of monomer blends, excess resin in the wash and activator tanks, which traditionally was disposed of in the sewers, can be separated easily and re-used.

Companies active in impregnation resins in the USA include Henkel-Loctite, Impco, Imprex, Chemence and Hernon. Chemence Inc. with manufacturing plants in the UK and USA, claims to be the North American market leader and supplies resin to some of its competitors. In Europe, Maldaner (Germany) and Ultraseal International (UK) are leading companies who compete with the European operations of Henkel-Loctite and Chemence and are aggressively expanding their operations into other parts of the world, including North America and the Far East.

It is estimated that around 3,400 tons of acrylic impregnation resins are used globally.

## References

1. C. Ruepping, inventor; DuPont Dow Elastomers, assignee; US Patent 6346300, 2002.
2. H.A. Flegel, *Auto Technology Magazine*, **5**, 64, 2002.
3. D.L. Kotzev, inventor; Chemence Inc., assignee; US Patent 6224622, 2001.



## 8 Consumption by Global Region and Material Type

### 8.1 Global Demand for Adhesives and Sealants

It is very difficult to quantify the global demand for adhesives and sealants from published reports because of different ways of reporting demand and decisions made on which products to include or exclude:

- North American figures often exclude adhesives such as formaldehyde based resins used in, for example, plywood and fibreboard production whereas these are reported in Asia. Asian figures often exclude starch adhesives used in corrugated bonding
- Adhesives used in carpet and nonwoven applications are usually excluded because the adhesives comprise a very high percentage of the finished product and act as key functional components. We report these adhesives as distinct categories.
- Porosity sealants are usually excluded, although they are important materials.

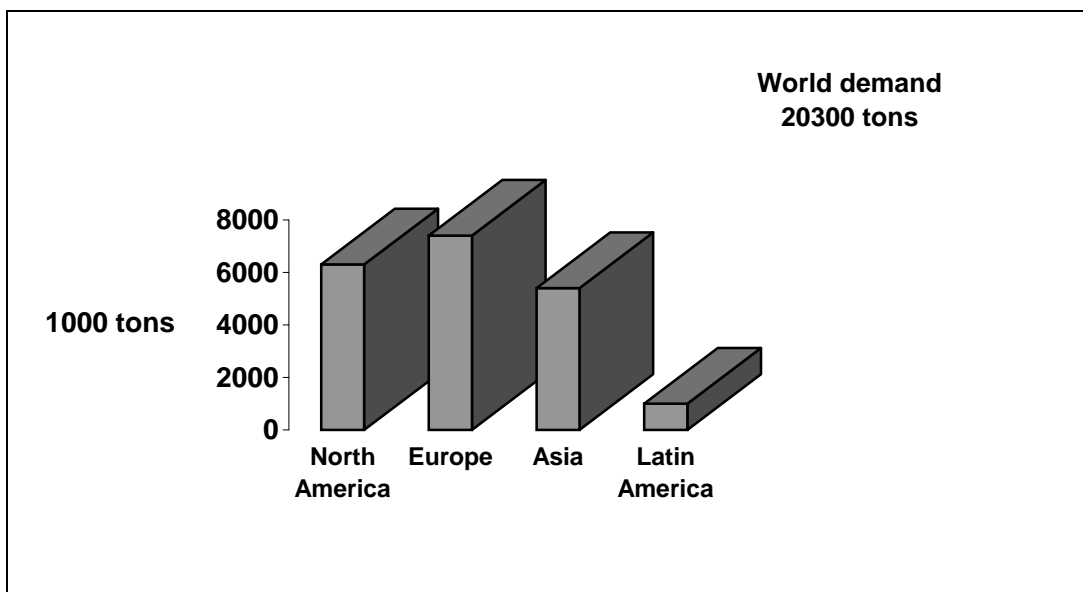
The numbers reported here include starches and formaldehyde-based adhesives, and come from various sources and in most cases have been built up from reported demands in various countries or regions. They do not include adhesives used for pressure sensitive applications, because most of the production of these is used captively by the large suppliers such as 3M and Avery Dennison.

#### 8.1.1 Global Adhesives

The global consumption of all commodity, speciality and high performance adhesives is 20 million tons with a value of over \$20 billion.

Table 8.1 and Figure 8.1 show the global demand for adhesives by region.

<b>Table 8.1 Global demand for adhesives by region</b>	
<b>Region</b>	<b>Demand 2001 (1000 tons)</b>
North America <sup>1</sup>	6500
Western Europe	7400
Far East <sup>2</sup>	5400
Latin America	1000
Total	20300
1. US, Canada, Mexico	
2. China, Japan, Taiwan and S. Korea	



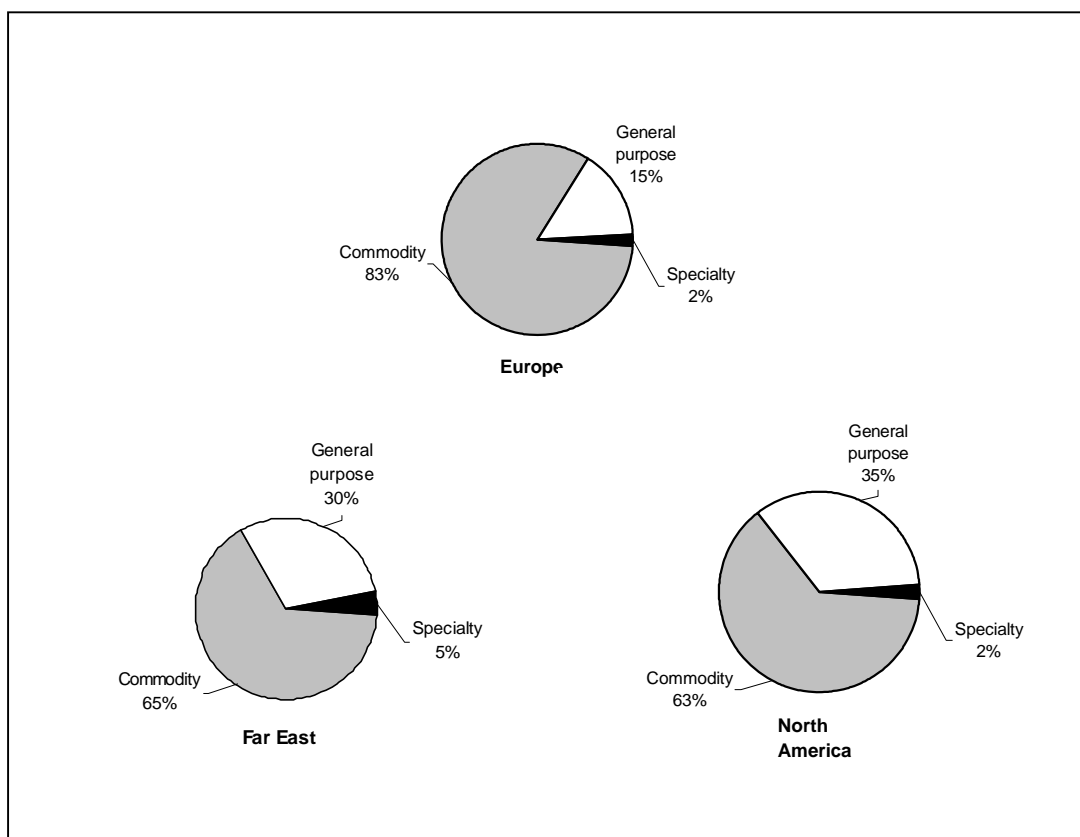
**Figure 8.1 Global demand for adhesives by region, 2001**

Table 8.2 shows the per capita consumption by region.

<b>Region</b>	<b>Demand (1000 tons)</b>	<b>Population (million)</b>	<b>Per capita demand (kg)</b>
North America	6500	406	16.0
Western Europe	7400	499	14.8
Asia	5400	2856	1.9
Latin America	1000	399	2.5

It can be seen that the per capita consumptions in North America and Western Europe are similar and that the consumptions in Asia and Latin America are very low in comparison. Much of the difference between North America/Europe and the rest of the world is probably accounted for by different preferences in, for example, packaging markets where the preponderance of primary, secondary and tertiary packaging in the food industry is contrasted by the use of a lot of less complex and recyclable packaging in, for example, the Far East. In, Asia, the per capita consumption is expected to rise dramatically over the next few years as food distribution becomes more sophisticated (requiring adhesively bonded packages) and there is a also a large increase in housing markets and in the production of consumer durables and non-durables. There is also considerable opportunity for growth in Latin America where consumption is dominated by the relatively advanced economies of Brazil and Argentina but increasing industrialisation in other countries in the region should spur growth.

Figure 8.2 shows the proportions of commodity, general purpose and speciality adhesives by region.



**Figure 8.2 Adhesive sales by region and adhesive type**

### 8.1.2 Global Sealants

The consumption of sealants is much lower than adhesives at around 665,000 tons (Table 8.3) with a value of \$3.5 billion.

Table 8.3 Global demand sealants	
Region	Demand 2001 (1000 tons)
North America <sup>1</sup>	273
Europe	219
Far East <sup>2</sup>	173
Total	665
1. US, Canada, Mexico	
2. China, Japan, Taiwan and S. Korea	

### 8.2 North America

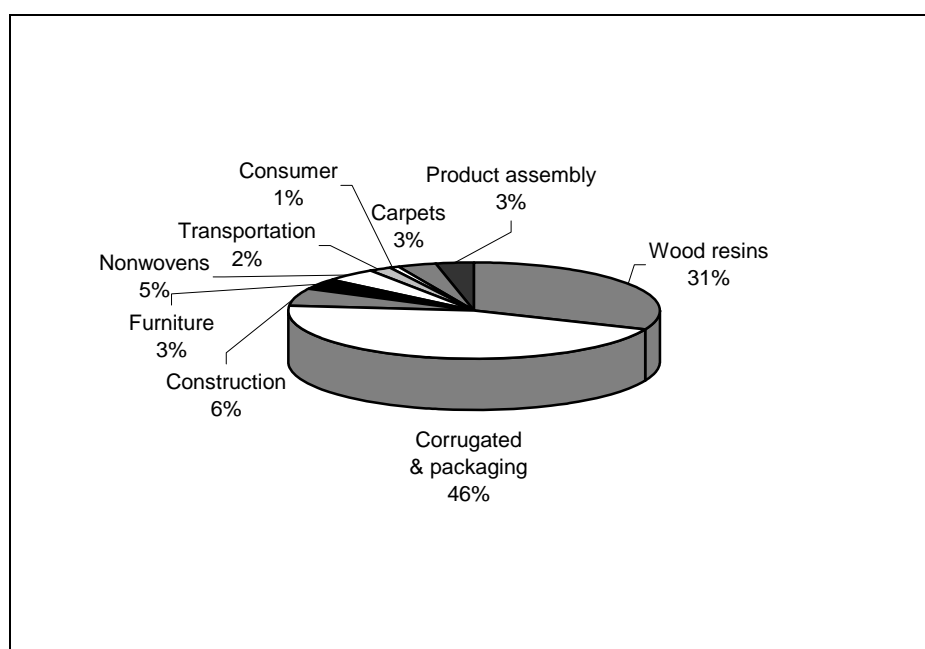
Table 8.4 shows the country breakdown of adhesives and sealants volume in North America.

Table 8.4 North American adhesive and sealant volumes (1000 tons)		
Country	Adhesives	Sealants
United States	6300	243
Canada	141	28
Mexico	80	2.3

Table 8.5 shows the demand for adhesives technologies in North America by adhesive type.

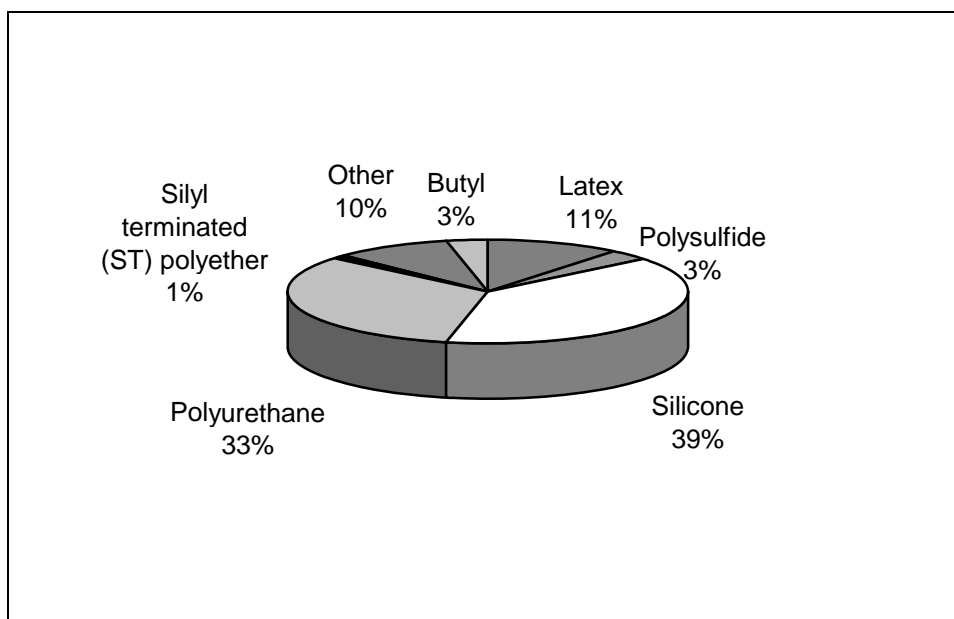
<b>Table 8.5 Adhesives demand in North America by type</b>	
<b>Type</b>	<b>Demand (1000 tons)</b>
PF, UF and MF	2180
Starch and dextrin	1660
Hot melt	550
Latex	1310
Solvent	410
Polyurethane	103
Other reactive adhesives <sup>1</sup>	50
1. Includes reactive acrylics, anaerobics, cyanoacrylates, UVs	

Figure 8.3 shows the demand for adhesives by application in North America.



**Figure 8.3 Demand for adhesives by application in North America**

Figure 8.4 shows the demand for sealants in North America. In contrast to other regions, the market is characterised by a large proportion of polyurethane sealants.



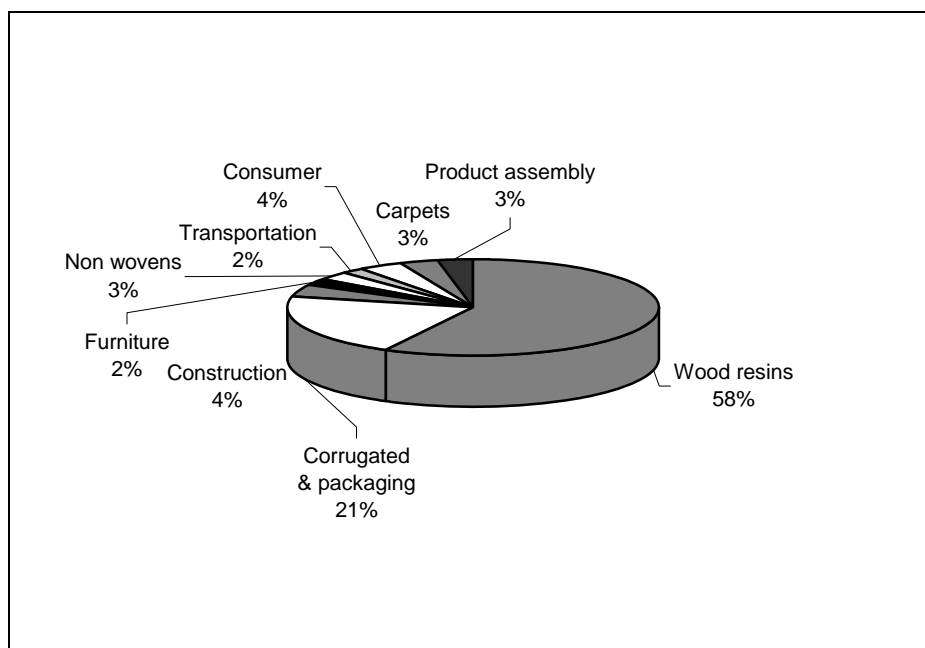
**Figure 8.4 Demand for sealant technologies in North America**

### 8.3 Western Europe

Europe is the largest market for adhesives, mainly because of a very large volume of formaldehyde-based products for wood resin bonding, particularly urea-formaldehyde resins for interior panels. Table 8.6 shows the demand for adhesives in Europe.

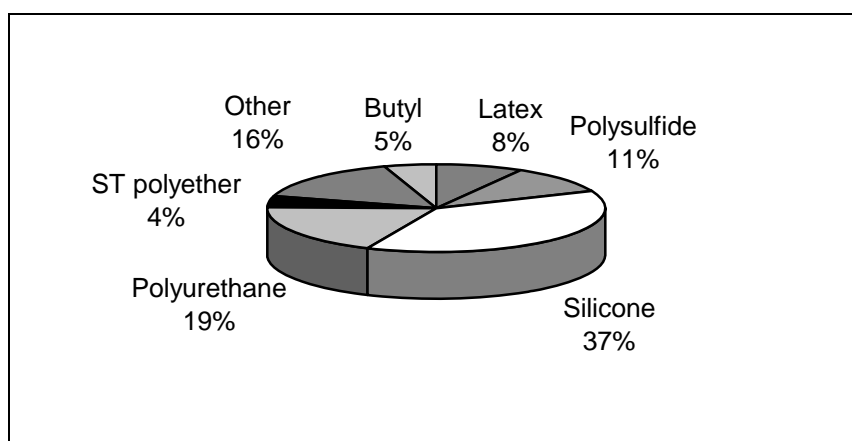
Table 8.6 Demand for adhesives in Europe	
Type	Demand (1000 tons)
PF, UF and MF	4470
Starch and dextrin	1600
Hot melt	257
Latex	652
Solvent	229
Polyurethane	113
Other reactive adhesives <sup>1</sup>	36
1. Includes reactive acrylics, anaerobics, cyanoacrylates, UVs	

Figure 8.5 shows the demand for adhesives by market segment.



**Figure 8.5 Demand for adhesives in Europe by market segment**

Figure 8.6 shows the demand for sealants by technology in Europe. In contrast to North America and the Far East, a high proportion of polysulfides are still used in Europe, although they are expected to come under serious competition in the construction market from silicones and urethanes.



**Figure 8.6 Demand for sealant technologies in Europe**

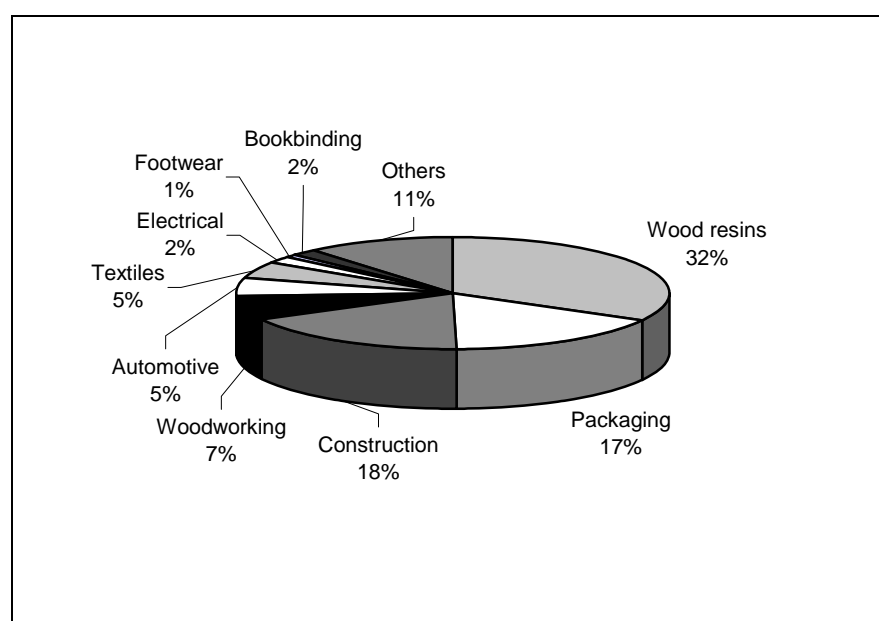
## 8.4 Far East

### 8.4.1 Japan

Table 8.7 shows the production of adhesives and sealants in Japan by type.

<b>Table 8.7 Production of adhesives and sealants in Japan by type</b>			
<b>Type</b>	<b>Production (1000 tons)</b>		
	<b>1998</b>	<b>1999</b>	<b>2000</b>
PF, UF and MF	346	349	342
Solvent based	72	68	70
PVA latex	144	135	138
Acrylic latex	62	52	51
VAE latex	34	36	34
Synthetic rubber latex	14	18	19
Misc. latex	31	36	37
Misc. water-based	8	7	7
Hot melt EVA	45	48	45
Hot melt PSA	34	37	36
Hot melt misc.	4	6	7
Epoxy	25	23	26
Polyurethane	51	54	60
Cyanoacrylate	1	1.2	1
Reactive acrylic	0.9	1.4	1.2
Misc. reactive adhesive	4.6	7.9	7.8
PSA-acrylic	65	71	100
PSA-rubber	81	60	64
PSA-misc.	5	12	8
Misc. adhesives	4.6	8	8.8
Industrial sealants	44	47	45
<b>Total</b>	<b>1086</b>	<b>1080</b>	<b>1112</b>
* Data from Japan Adhesives Industries Association			

Figure 8.7 shows the demand for adhesives by market segment.



**Figure 8.7 Demand for adhesives in Japan by market segment**

Japanese government statistics show the market for construction sealants (Table 8.8).

<b>Table 8.8 Consumption of construction sealants in Japan, 2000</b>		
<b>Type</b>	<b>1000 tons</b>	<b>% share</b>
Silyl terminated polyether	40	39
RTV silicone	27	26
Polyurethane	29	28
Polysulfide	7	7
Total	103	

The demand for adhesives in Japan has been flat over the last few years, reflecting general economic conditions in that country and the shift of some manufacturing operations to other Asian countries.

#### **8.4.2 China**

The adhesives and sealants industry is one of the fastest developing sectors of the Chinese chemical industry. From 1995 to 2000 the average annual increase in adhesive products was over 12% [1].

Use of formaldehyde based resins for plywood construction is the largest segment by volume, ca. 60%, construction ranks second at 22%, followed by packaging and shoe manufacturing at 6.2% and 4% respectively. The consumption of adhesives in automotive, electrical and electronics is increasing rapidly.

Table 8.9 shows the growth in Chinese production of adhesives and sealants from 1996 through 2000. Since the difference between total exports and imports of these products is a little over 120,000 tons, these production figures are close to consumption figures.

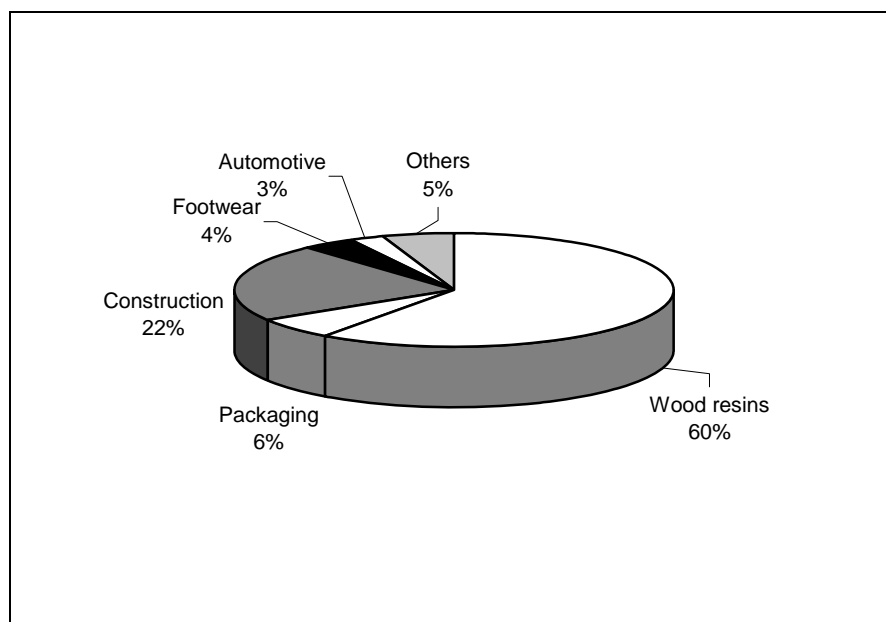
<b>Table 8.9 Production of adhesives and sealants in China 1996-2000</b>					
<b>Type</b>	<b>Production (1000 tons)</b>				
	1996	1997	1998	1999	2000
PF, UF and MF	543	769	933	995	1060
PVA latex	215	247	279	308	340
Acrylic latex	166	197	280	330	370
VAE latex	25	44	43	43	49
Polychloroprene	123	208	219	205	210
Polvinyl formal and butyral	200	200	195	185	167
Polyurethane	32	38	50	111	124
Epoxy	10	16	17	25	30
Hot melt	13	28	33	31	36
Hot melt PSA	-	-	-	16	22
Silicone	8	12	15	18	23
Polysulfide	1.5	1.5	2.1	2.4	2.6
Cyanoacrylate	0.6	0.8	1.3	1.35	1.5
Anaerobics		0.15	0.21	0.25	0.29
Total	1338	1763	2067	2270	2435

Environmentally friendly latex, hot melt adhesives and hot melt PSAs are becoming more important in the market. The production of acrylic latex, PVA latex and VAE latex amounted to 759 thousand tons in 2000, an increase of 11.45% over 1999. The production of hot melts amounted to 56 thousand tons in 2000, an increase of 23.4% over 1999. It is projected that these types of adhesives will continue to grow at 11-12% p.a.



Solvent based polychloroprene adhesives are very popular in internal decoration, wood processing and shoe manufacture. They are being replaced by polyurethane adhesives and hot melt adhesives because of concerns over solvent emissions.

Figure 8.8 shows the demand by market segment.



**Figure 8.8 Demand for adhesives and sealants in China by market segment**

As the Chinese standard of living improves and the economy grows, it is projected that higher performance adhesives and sealants will become more important including:

- Water-borne polyurethanes for laminating and internal decoration
- Reactive urethanes and RHMU for automotive lights and windshield installation
- Reusable PSA for notepads, high strength PSA tapes
- Medical PSA products
- Structural adhesives for aerospace and automotive
- Adhesives for electronics
- Silicone adhesives, silicone PSA

The China Chemical Reporter estimated that during 2000 consumption of adhesives and sealants by the automotive industry in China was estimated to reach 63,700 tons with projections to reach 100,000 tons in 2010. The 2000 market breakdown by adhesive type is given in Table 8.10.

<b>Table 8.10 Demand for automotive adhesives and sealants in China (tons)</b>		
	<b>Demand 2000</b>	<b>2010 projected</b>
PVC plastisols	19,800	47,400
Heat insulating primer	14,400	24,460
Polychloroprene	12,400	29,700
Butyl	2,030	4,870
SBR	1,400	360
Nitrile	1,070	2,560
Polysulfide	730	1,750
Polyurethane	620	1,480
Epoxy	840	2,010
Acrylic	315	830
<b>Totals</b>	<b>63,700</b>	<b>100,000</b>

The adhesives and sealants industry in China is transitioning from an incredibly fragmented structure of over 1500 local manufacturers to one which has a very strong presence from multinational corporations, combined with joint ventures. Multinational companies with operations in China include Henkel, Henkel-Loctite, 3M, Avery Dennison, H.B. Fuller, National Starch, Bostik Findley and Rohm & Haas.

## 8.6 Latin America

In the mid 1990s, demand for adhesives and sealants rose at a slower rate in Latin America than in North America and Europe, suggesting opportunity for mid-term growth, according to a study by the Freedonia Group, Cleveland.

The study indicated that regional demand will grow from 885,000 tons in 1997 (the equivalent of a per capita consumption level of 2.2 kilograms) to 1.1 million tons by 2002. Among leading consumers of adhesives are Brazil and Argentina, followed by Chile, Colombia and Venezuela, reflecting the size of their populations (Table 8.11) and relative degrees of industrialisation.

<b>Table 8.11 Latin American populations</b>	
	Population (million)
Argentina	36
Brazil	162
Colombia	41
Venezuela	23
<b>Subtotal</b>	<b>252</b>
Peru	25
Chile	15
Ecuador	12
Bolivia	8
Paraguay	5
Uruguay	3
Caribbean	35
Central America	34
<b>Subtotal</b>	<b>137</b>
<b>Total</b>	<b>399</b>

Freedonia projects the 2002 market at \$1.1 billion. The company projects the value of the market in 2007, when volume is expected to reach 1.4 million metric tons, at about \$1.6 billion.

Leading adhesives markets include paper and packaging, consumer products and consumer non-durables.

Long-term, the Latin American market is attractive for North American and European adhesive producers. The growth in GDP for the region is expected to be higher than that for North America and Western Europe.

## Reference

1. M.X. Yang, *Adhesive Technology*, 2000, **17**, 3, 8.

## 9 Industry Structure and Key Players

### 9.1 Raw Material Suppliers

#### 9.1.1 Acrylics

UCB, Atofina's Sartomer and Cray Valley subsidiaries, and Cognis are the three largest monomer and oligomer producers. Other leading participants include BASF, Akzo Nobel's Akcros Chemicals and Ciba Specialty Chemicals. Speciality producers in the US include Bomar and Bimax. In Japan, Toagosei is a leading producer of monomers and oligomers and Hitachi Chemical supplies speciality monomers.

#### 9.1.2 Epoxies

The epoxy adhesives industry is very fragmented worldwide with probably thousand of formulators. Historically, this situation was encouraged by the three major suppliers of the basic resins, Dow Chemical, Shell Chemicals and Ciba Geigy who sold resins and hardeners but were not forward integrated (although Ciba did have small adhesives and tooling resin divisions). This situation has changed somewhat in recent years with Dow Chemical becoming an adhesives supplier through its Dow Automotive division, and Ciba selling off its resin and adhesive division, now both under the Vantico name. The Shell Chemicals business, also sold and, called Resolution Performance Products (RPP), remains a raw material supplier. These big 3 suppliers dominate the supply situation in both North America and Europe and Dow and RPP are backward integrated into bisphenol A, a key intermediate for epoxies.

In the Far East, there are five major resin suppliers in Japan, JER (joint venture (JV) of RPP and Mitsubishi), Asahi Kasei Epoxy (former JV between Asahi and Ciba Geigy), Tohto Kasei, Nagase and Dainippon Ink. Other important suppliers are Nan Ya Plastics (Taiwan), Kukdo Chemical (Korea) and Thai Epoxy (Thailand).

#### 9.1.3 Latex

SBR is the largest volume latex product produced globally and there are many other manufacturers. BASF and Dow Reichhold have the leading global market shares. Other important suppliers include Omnova Solutions and Ameripol Synpol (US), Polimeri Europa and Polymer Latex (Europe), with JSR, Zeon, Nippon A&L, Korea Kumho and Taiwan Synthetic being major suppliers in the Far East.

BASF is the leading producer of acrylic emulsions with a 400,000 ton plant in Western Europe and a 140,000 ton plant in Finland. Rohm & Haas and Dow Chemical are also major players in acrylic emulsions.

Manufacturers of nitrile latices are BASF, PolymerLatex, Dow Reichhold, Zeon, Noveon and Synthomer.

There has been considerable consolidation of manufacturers and plants in polychloroprene latex in recent years with DuPont Dow Elastomers being the only manufacturer in North America with Polimeri Europa (Enichem) and Bayer, the only ones in Europe. Japanese producers are Denki Kagaku Kogyo, Tosoh and Showa DDE.

National Starch and Air Products Polymers are the leading manufacturers of vinyl acetate emulsions. Air Products Polymers is the global market leader in VA/E emulsions with Clariant holding the leading share in Europe

#### **9.1.4 Formaldehyde Resins**

Formaldehyde capacity has always exceeded demand by a substantial margin and this situation will continue.

Borden Chemical is the world's largest producer of formaldehyde resins with a production of over 2.2 million tons of formaldehyde.

About 60% of this total is used captively for resin production. The rest is sold to customers on the merchant market. Other major producers include Celanese, Georgia Pacific, Neste and Perstorp.

#### **9.1.5 Silicones**

The major producers of silicone hydrosylate, the key building block for silicones, are Dow Corning, GE Silicones and Wacker.

#### **9.1.6 Polyurethanes**

The polyol industry is both concentrated and global. In the United States, the six largest producers represent 89% of total capacity, and in Western Europe and Japan, the six largest companies account for 85% and 76% of the business, respectively.

Dow Chemical is the largest worldwide producer of polyether polyols, with the largest number of both plants and capacities in the greatest number of countries. Lyondell Chemical (now a part of Bayer) is the second-largest producer, with plants in the United States, Europe and Asia.

The largest producers of isocyanates are Bayer, Dow Chemical, Enichem, ICI and BASF.

### **9.2 Adhesive and Sealant Manufacturers**

The industry has been changed significantly over the last few years by a series of mergers and acquisitions. Table 9.1 lists the major restructuring.

Although some analysts regard this industry as highly consolidated, it is in fact still quite fragmented on both a global and regional basis.

**Table 9.1 Recent restructuring in the adhesives and sealant industry**

<b>Companies</b>	<b>Description</b>
Forbo AG	Purchased Swift Adhesives from Reichhold Inc.
Bemis Inc.	Purchased Kanzaki's pressure sensitive materials
UPM-Kymmene	Purchased MACtac PSA business from Bemis Inc.
3M	Acquired urethane adhesive manufacturer Polymer Engineering Corp.
Rohm & Haas	Acquired Morton International
Rohm & Haas	Acquired Technical Coatings from Benjamin Moore, giving it the Coseal line of cold seal adhesives
Rohm & Haas	Purchased the rubber-to-metal bonding business of Chemetall Company of Frankfurt, Germany
Henkel	Purchased the outstanding 50% of the shares in Liofol, the JV between Henkel and Lord Corp. in laminating adhesives
Henkel	Purchased Cemedine USA, Inc., supplier of automotive adhesives and sealants
Henkel	Purchased Solypast SA, Barcelona, Spain a manufacturer of D.I.Y adhesives and sealants
Henkel	Purchased Sellotape from Verdoso Holdings Ltd. (UK)
PPG	Purchased PRC-DeSoto, formerly Courtaulds Aerospace Sealants
Vantico	Former epoxy resins business of Ciba Specialty Chemicals was sold to Morgan Grenfell Private Equity (London)
Vantico	Purchased the Agomet and Atlas Adhesives and Tooling business of the Degussa Business Unit, Röhm Specialty Acrylics
Bostik Findley	Formed by the merger of Total and Elf Atochem
Sovereign Specialty Chemicals Inc.	Purchased adhesives business of Croda International and also Imperial Adhesives
Henkel Loctite	Acquired Dexter Dexter's \$205 million speciality polymer business which includes aerospace adhesives
Bakelite AG	Acquired epoxy resin business of LG Chem in South Korea
Dow Automotive	Acquired Gurit-Essex AG
Avery Dennison	Acquired the Adespan pressure-sensitive materials operation of Panini SpA (Italy)
Quest Specialty Chemicals Inc.	Acquired the adhesives and sealants division of Uniroyal Technology Corp., renamed Royal Adhesives & Sealants
RPM	Purchased DAP
GE Silicones	Acquired Macklanburg-Duncan's adhesives and sealants business.

### **9.2.1 The Big Companies**

A handful of large companies now hold a very large global market share.

These leading companies are Henkel, Avery Dennison, H.B. Fuller, 3M, Bostik-Findley, National Starch, Sika and UPM-Kymmene, all with sales over \$1 billion (Table 9.2).

<b>Table 9.2 The big adhesive and sealant companies</b>		
<b>Company</b>	<b>Headquarters</b>	<b>Sales, \$million</b>
Henkel	Germany	2700
3M	US	2000
Avery Dennison	US	2100
H.B. Fuller	US	1200
Bostik Findley	France	1000
Borden Chemicals	US	1000+ <sup>1</sup>
Sika AG	Switzerland	1200
UPM-Kymmene	Finland	1100
National Starch	UK	1100
1. Estimated, Borden sells PF, UF and MF resins		

The total sales of these companies are close to \$13 billion.

Henkel Group's Adhesives business sector is number one on the world market with sales of \$2.7 billion after its major acquisitions of Loctite and Dexter. Its three strategic business units are Consumer and Craftsmen Adhesives, Engineering Adhesives (Loctite) and Industrial Adhesives and Sealants. These acquisitions have had a significant positive impact in profit margins. Loctite's engineering adhesives are high value products with excellent margins. Loctite's gross margins were close to 60% of sales prior to its acquisition by Henkel with income at around 20%.

3M does not release its adhesives sales figures. Merrill Lynch estimates 3M's adhesives division (hot melts, epoxies, and urethanes) at \$350 million, and its two-sided tapes and hook and loop fasteners business at \$350 million. The masking tape and specialties business and the packaging systems business are estimated at \$600 million each. Banc of America Securities (New York) estimates those businesses at about \$700 million each.

Bostik Findley's business, formed by the merger of Total and Elf Atochem is now a major international supplier with sales over \$1 billion. 60% of its sales are in Europe and 30% in North America.

The Finnish company UPM-Kymmene Corporation acquired MACtac, the pressure sensitive materials business, from the US based Bemis Company Inc. The acquisition by UPM-Kymmene strengthens the global business operations of its PSA label stock subsidiary, Raflatac and gives it global sales of \$1.1 billion.

### 9.2.1 2nd Tier Companies

A second tier of large companies has global sales in the \$300-700 million range (Table 9.3).

<b>Table 9.3 2nd tier adhesive and sealant companies</b>		
<b>Company</b>	<b>Headquarters</b>	<b>Sales, \$million</b>
Rohm & Haas	US	660
Intertape Polymer	Canada	600
Dow Automotive	US	600
Georgia Pacific	US	500
Tremco	US	450
Forbo AG	Switzerland	375
Sovereign	US	350
Dow Corning	US	? <sup>1</sup>
General Electric	US	? <sup>1</sup>
1. Do not publish adhesive and sealant sales. We estimate their sales in the \$300-700 million range		

Rohm & Haas became a large supplier after its acquisition of Morton, as did Dow Automotive with its acquisition of Gurit-Essex

Forbo's acquisition of The Swift adhesive business from Reichhold, has turned it into a major adhesive company with sales of approximately \$375 million.

GE Silicones, a major RTV silicone supplier purchased Macklanburg-Duncan's (M-D; Oklahoma City) adhesives and sealants business and formed a new subsidiary, GE Sealants & Adhesives.

Tremco, with \$450 million/year in sales, aims to hit \$1 billion within five years. It is pushing into original equipment manufacture for automotive applications. Silicone sealants and adhesives for intricate automotive wiring are among the OEM applications where growth of 20%-25%/year is expected.

Sovereign Specialty Chemicals increased its sales by 40% this year through its acquisitions of Imperial Adhesives from NS Group (Newport, KY) and Croda's (UK) adhesives business. The company's sales are now at about \$350 million/year.

### **9.2.3 Other Leading Companies**

There are many companies of significant size all over the world. Many of these specialise in specific technologies or markets.

Examples are:

- Vantico, the former Ciba Geigy unit, who market speciality epoxies and polyurethanes
- Chemence (US & UK) specialising in anaerobics and cyanoacrylates
- Three Bond (Japan) in anaerobics
- Toa Gosei (Japan) in cyanoacrylates
- Elmers Products (US) with latex and cyanoacrylates
- Lord Corporation (US) with rubber adhesives and acrylics
- ITW(US) – owns Plexus, Devcon and Fiberglass Evercoat
- Kommerling (Germany) in automotive products
- PPG Aerospace with aerospace sealants

Table 9.4 shows leading manufacturers and formulators of different adhesives and sealants types. This directory includes companies known to manufacture the basic adhesive or formulate the different types of adhesives. It does not include companies who are solely distributors or re-packagers. Some adhesives, e.g., epoxies, are manufactured by hundreds of companies and only the largest companies are identified.

**Table 9.4 Manufacturers of adhesives and sealants by type (country)**

<b>Anaerobics</b> Chemence (US/UK) Cyberbond (US, D) Devcon (G) Henkel-Loctite (G) Hernon Loxeal (IT) Three Bond (J)	<b>Cyanoacrylates</b> Alteco (J) Asia Tong Shen (TW) Chemence (US/UK) Cyberbond (US, D) Elmers Products (US) Henkel-Loctite (G) Hyloc (UK) Koatsu Gas (J) Loxeal (IT) Pacer Technology (US) Palm Laboratories (US) Permabond (G) Taoka Chemical (J) Three Bond (J) Toagosei (J)	<b>Hot Melts (EVA)</b> 3M (G) Beardow & Adams (UK) Bostik Findley (G) Forbo (CH, US) H.B. Fuller (G) Jowat (US, D) National Starch (G)
<b>Reactive acrylics</b> 3M (G) Chemence (US/UK) Dymax Corp. (US) Henkel Loctite (G) IPS Corp. ITW Plexus (US) Lord Corp. (G)	<b>UF and MF Resins</b> Borden Chemical (G) Georgia Pacific (US) Neste (OY) Seaco	<b>Hot melts-reactive</b> Bostik Findley Forbo (CH) HB Fuller(G) Henkel (G) Jowat (US) Kleiberit (D) National Starch (G) Rohm & Haas (G)
<b>UV adhesives</b> DSM Desotech (US/J/N) Dymax Corp. (US) Henkel-Loctite Three Bond (J) Wellomer (D)	<b>Polyurethane</b> 3M (G) Ashland (G) Bostik Findley (G) Chemique (UK) Dow Automotive (G) Henkel (G) Rohm & Haas (G) Sika (G) Tremco (G) YH America (US/J)	<b>Hot melts-PA/polyester</b> Arizona Chemicals (US) Atofina (G) Bostik Findley (G)
<b>Pressure sensitives</b> 3M (G) AdhesivesResearch (US) Air Products (G) Avery Dennison (G) Ashland (G) Biersdorf/Tesa (G) FLEXcon (US, UK) Intertape Polymer (CA, US) National Starch (G) Nitto Denko (G) Raflatac (G) Rohm & Haas (G) Tyco (US)	<b>Phenolics</b> Ashland Bakelite AG (G) Borden Sovereign Sumitomo Bakelite (G)	<b>Epoxy</b> 3M (G) Alteco (J) Bakelite AG (G) Dow Automotive (G) Henkel-Loctite (G) Sumitomo Bakelite (G) Vantico (G)
<b>Silicones</b> Accumetric (US) Dow Corning (G) GE Silicones (G) Kisling AG (CH) Makroflex (E, OY) May National (US) NuSil (US) Rhodia Three Bond (J) Tremco (US) Wacker Silicones	<b>Polysulfides</b> Akcros Chemicals (G) Chemetall (D) Colfirmit Rajasil (D) Fenzi (IT) Henkel Teroson (D) Kömmerring (D) Polyspec (US) PRC-DeSoto (US) Toray (J)	<b>Casein</b> American Casein Borden Chemical (G) National Casein (US) Lactalis Ind. (F/US)
		<b>Butyl</b> Bostik Findley (G) Fenzi (IT) HB Fuller (G) Tremco (G)
		<b>Latex</b> Air Products Polymers (G) Avery Dennnison (G) Dow Chemical (G) Elmers Products (US) Omnova (US) Rohm & Haas (G) Sovereign (US)
<b>Country legend:</b> CA – Canada CH – Switzerland D – Germany E – Estonia F – France G - Global company, multiple locations IT – Italy N – Netherlands OY – Finland US – USA		



### **9.3 Distribution**

Many industrial and automotive adhesives and sealants are sold direct to the end-users, although certain countries, notably the US and the UK have speciality adhesives distributors and sophisticated industrial supply distribution networks. Marine products are also sold through full-line speciality marine distributors.

In addition to the car dealer network, the US has a very strong distribution network to the automotive aftermarket, including speciality automotive suppliers and a retail segment.

Adhesives and sealants for the construction industry are distributed through:

- building materials wholesale distributors
- roofing, siding, insulation wholesale distributors
- window and door wholesale distributors
- lumber yards
- hardware stores
- home centres

Consumer adhesives are sold in hardware stores, food stores, drug stores and mass merchandisers.



## 10 International Trends and Conclusions

There has been considerable consolidation in the industry over the last 10 years. Some of this has been aggressive global expansion by large companies and some caused by increasing consolidation in the customer base. However, the industry is still very fragmented with an estimated three to four thousand suppliers worldwide. We will continue to see the industry giants acquiring smaller specialist or regional manufacturers to establish a market position or gain a specific technology.

A consequence of these large mergers has been that most of the large companies are now full-line suppliers, offering most if not all of the available adhesive and sealant technologies. This makes it increasingly difficult for customers to differentiate between suppliers. Gone are the days when one could associate say, Ciba Geigy with epoxies, or Loctite with anaerobics, or Sika with polyurethanes.

The economies of scale and worldwide purchasing power of these large companies should help to lower their costs and maintain pricing for their customers.

However, a natural corollary of these mergers is the stifling of innovation and the intense market focus that exists in smaller companies. However, all is not lost for the industry. We will continue to see startup companies, specialising in a specific technology or niche market, because manufacturing of adhesives is a relatively simple process. One can purchase a mixer, buy chemicals on the open market, add a pinch of creativity and create a good business (until the time you get acquired by one of the giants!).

Growth in adhesives and sealants will be influenced by increases in the global GDP and by the growth of the individual end-user market segments.

### 10.1 Market Drivers

*Global Market* – The overall market is global and very large and is spread across a wide range of both industrial and consumer markets.

*Regional expansion* – High growth is expected in China and Latin America.

*Growth in key segments* – There are high growth rates in several markets, e.g., the housing market, medical, packaging and automotive.

*Replacement of solvent-based systems* – Worldwide legislation on solvent emissions will create more opportunities for hot melt latex and other water-based systems to replace solvent based adhesives and sealants.

*100% solid systems* – technologies such as hot melts, reactive acrylics and UV systems will grow because of their safety and energy efficiency.

*Replacement of other fastening methods* – adhesives will continue to replace mechanical fastening systems due to better performance and overall lower costs.

*High performance sealants* – architects increasingly specify silicones and polyurethanes in place of preformed seals because of their ease of application, high performance and durability.

### 10.2 Market Restraints

*Economic cycles* – certain market segments are in low growth or declining modes, e.g., the commercial aerospace industry and telecommunications, while others are influenced strongly by macroeconomic cycles, e.g., the automotive and construction industry.

*Automotive and carpet industries* – customer consolidation has led to intense pricing pressures on suppliers.

*Nonwoven industry* – replacement of adhesives by thermal bonding and hydro entanglement technology.

*Raw material prices* – recent increases in raw materials prices are a major concern, particularly to suppliers in price sensitive markets like wood resins and carpet adhesives.

### **10.3 Individual Market Sectors**

Packaging will continue to consume large volumes of adhesives and food packaging, which is recession-proof, will be the major driver of growth.

Construction markets are expected to continue to consume greater volumes of adhesives and sealants due to low interest rates in the West stimulating new construction.

The medical industry is recession-proof and more speciality adhesives will be used to assemble medical devices and in surgical applications.

The commercial aerospace industry will continue in decline for some years, although increased military construction will be a short term saviour for suppliers to this industry.

Use of adhesives and sealants in the appliance industry has been growing significantly but is vulnerable to inflation and recession. For major appliances, replacement demand accounts for about 75% of all purchases, and the remainder is tied to the building of new homes. With the majority of appliance sales consolidated among a few large suppliers, the industry is extremely competitive and under constant price pressure.

Industry consolidation has been dramatic in many sectors, but none more so than in automotive. In 1997 there were 23 global key car manufacturers. By the year 2000 this had fallen to 9 via a series of mergers and acquisitions. The prediction is that by 2010 this could fall further to 5 global manufacturing giants.

By 2010, the industry expects that the number of global Tier 1 suppliers will fall from the current 600+ worldwide to 30. Tier 2 numbers will collapse from 10,000+ to 800.

This will create severe price pressures on suppliers and the successful adhesive manufacturers will need to be technology leaders, global in scale and have close alliances with the OEMs and key Tier 1 suppliers.

According to the Freedonia Group, demand for adhesives used in the automotive industry is forecast to increase 1.9% per year to reach more than 670,000 metric tons in 2002. Another market research company, Frost & Sullivan, contends that the advanced automotive adhesives market in North America will grow to \$277.8 million in 2003.

Although electronics markets were depressed in 2001 and 2002, large growth is projected in many electronics applications. For example, global demand for flip chips is forecast to grow significantly and has grown from 660 million units in 1998 to 2.7 billion in 2002. Computers use 30% of all chips but the wireless phone market is the fastest growing segment.

Tables 10.1 and 10.2 show projected trends in adhesives and sealants technologies respectively.

<b>Table 10.1 Trends in adhesive technologies</b>		
<b>Technology</b>	<b>Trend</b>	<b>Market drivers (D) and restraints(R)</b>
Wood resins	Moderate growth	<b>D</b> Strong housing market <b>R</b> Increase in raw material prices
Starch and dextrin	Strong growth	<b>D1</b> Growth of global packaging market <b>D2</b> Growth of Asian packaging market <b>R</b> Competition from synthetic resins
SBR	Flat	<b>D</b> Growth of PSA market <b>R1</b> Decline in supply base <b>R2</b> Price pressures from carpet manufacturers <b>R3</b> Competition from acrylics in PSAs
Vinyl ester latex	Strong growth	<b>D1</b> Growth in housing market <b>D2</b> Growth in PSAs <b>D3</b> Growth in packaging <b>R</b> Competition from acrylics
Acrylic latex	Strong growth	<b>D1</b> Growth of PSA market <b>D2</b> Strong housing market <b>R</b> Increase in raw material prices
Solvent-based	Steady decline	<b>D</b> No known drivers <b>R</b> Replacement by safer technologies
Hot melts	Strong growth	<b>D1</b> Replacement of solvent adhesives <b>D2</b> Growth in RHMUs <b>R1</b> Competition from acrylic latex <b>R2</b> High equipment costs restrictive for small users
Polyurethane	Strong growth	<b>D</b> Growth in construction, packaging and industrial uses <b>R</b> Competition from acrylic latex
Polychloroprene	Slow decline	<b>D1</b> Latex will replace solvent-based versions <b>R1</b> Less use in footwear industry <b>R2</b> Continued government legislation and activist pressures on chlorine-containing materials
Reactive acrylic	Strong growth	<b>D1</b> Expiration of patents will encourage new market entrants <b>D2</b> Growth in electronics <b>R</b> Concerns over methyl methacrylate odour and flammability
Epoxy	Moderate growth	<b>D1</b> Increased structural bonding in automotive <b>D2</b> Growth in electronics <b>R1</b> Depressed aerospace market <b>R2</b> Competition from urethanes and acrylics
Anaerobic	Moderate growth	<b>D</b> Growth in global GDP <b>R</b> Lowering of profitability with many new market entrants
Cyanoacrylates	Moderate growth	<b>D1</b> Increase in consumer market <b>D2</b> Increase in medical applications <b>R</b> Lowering of profitability with many new market entrants
UV adhesives	Moderate growth	<b>D1</b> Growth of flexible packaging applications <b>D2</b> Growth in electronics <b>R</b> Competition from urethanes and acrylics

<b>Table 10.2 Trends in sealant technologies</b>		
<b>Technology</b>	<b>Trend</b>	<b>Market drivers (D) and restraints(R)</b>
RTV silicones	Strong growth	<b>D1</b> Growth in housing market <b>D2</b> Growth in automotive electronics sealing <b>R</b> Competition from polyurethanes and acrylic latex
Polyurethane	Strong growth	<b>D1</b> Growth in construction <b>D2</b> Growth in flexible packaging <b>R</b> Inability to give durable bonds to glass
SBR latex	Flat	<b>D</b> Growth in housing market <b>R1</b> Replacement by acrylic latex <b>R2</b> Decline in supplier base
Acrylic latex	Strong growth	<b>D1</b> Growth in construction <b>D2</b> Growth in DIY sealants <b>R</b> High price compared to other latices.
Solvent based	Steady decline	<b>D</b> Low cost will maintain some applications <b>R</b> Replacement by safer technologies
Oil based	Steady decline	<b>D</b> Low cost will maintain some applications <b>R</b> Replacement by better technologies
Butyl	Moderate growth	<b>D</b> Growth of adhesives market <b>R</b> Replacement by silicones and polyurethanes
Polysulfide	Slow decline	<b>D</b> Growth in housing market <b>R1</b> Depressed aerospace market <b>R2</b> Competition from silicone and polyurethane
Silyl-terminated polyethers	Strong growth	<b>D</b> Increased use in Europe <b>R</b> Poor acceptance in North America because of incumbent silicones and urethanes
Acrylic impregnation resins	Moderate growth	<b>D</b> Growth in electronics sealing <b>R</b> Very dependent on automotive industry

Improved technologies and a growing emphasis on environmentally friendly materials and products are among the factors that will affect the global market for adhesives and sealants in this decade.

Adhesives companies must define their strategic objectives clearly if they are to survive in the current competitive climate. They must define whether they are in high volume commodity products, general purpose, or speciality products in niche markets, and then adjust their manufacturing, technology and marketing strategies to suit their goals.

If the focus is on high volume markets then items such as cost and brand recognition will be important considerations, but if niche markets are the focus then innovation and performance will be more important.

The overall prospects for adhesives and sealants remain positive. These seemingly products of low significance are in fact critical components of modern society, affecting the quality and safety of our food, the performance of our cars and aeroplanes and the assembly of literally millions of industrial and household items. Adhesives and sealants are usually an insignificant factor in the overall cost of a product but can have dramatic effects on the productivity of an operation and the quality of a product.

The winners in this industry will not be those that only try to reduce the costs of adhesives or sealants – internal competition in the adhesives industry will take care of that – but those who continually innovate in all aspects of their operations and strive to find newer, better and faster products that will dramatically influence the cost-effectiveness of a customers' operation or products.

We expect to see more global branding of products as manufacturers seek to build loyalty to well respected brands.

Companies will do well to remember that great products build great brands and not necessarily vice versa.





## **11 Associations and Media**

### **11.1 Associations**

Adhesives & Sealants Council (US)	<a href="http://www.ascouncil.org">www.ascouncil.org</a>
Adhesives Manufacturers Association (US)	<a href="http://www.adhesives.org/ama">www.adhesives.org/ama</a>
The Adhesion Society (US)	<a href="http://www.adhesionsociety.org">www.adhesionsociety.org</a>
AFERA – European Association for the Self Adhesive Tape Industry	<a href="http://www.amera.com">www.amera.com</a>
FEICA – Association of European Adhesives Manufacturers	<a href="http://www.feica.com">www.feica.com</a>
FINAT – Worldwide Association for Self Adhesive Labels and Related Products	<a href="http://www.finat.com">www.finat.com</a>
INDA – Association of the Nonwoven Fabrics Industry	<a href="http://www.inda.org">www.inda.org</a>
Pressure Sensitive Tape Council (US)	<a href="http://www.pstc.org">www.pstc.org</a>
Japan Adhesives Industries Association	<a href="http://www.jaia.gr.jp">www.jaia.gr.jp</a>
Sealant, Waterproofing & Restoration Institute (US)	<a href="http://www.swrionline.org">www.swrionline.org</a>
Society for Adhesion and Adhesives	<a href="http://www.me.ic.ac.uk/materials/SAA/SAA1.html">www.me.ic.ac.uk/materials/SAA/SAA1.html</a>
TAPPI – Technical association for the worldwide pulp, paper, and converting industry (US)	<a href="http://www.tappi.org">www.tappi.org</a>
Tag and Label Manufacturers Institute, Inc. (US)	<a href="http://www.tlmi.com">www.tlmi.com</a>

### **11.2 Media**

Adhasion Kleben & Dichten	<a href="http://www.klebendichten.com">www.klebendichten.com</a>
Adhesives Age	<a href="http://www.adhesivesage.com">www.adhesivesage.com</a>
Adhesives & Sealants Industry	<a href="http://www.adhesivesmag.com">www.adhesivesmag.com</a>
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Journal of Adhesion Science and Technology	<a href="http://www.vspub.com">www.vspub.com</a>

## Abbreviations and Acronyms

ABS	acrylonitrile-butadiene-styrene terpolymer
ACA	US Automotive Composites Alliance
ACM	acrylic rubber
AEM	ethylene-acrylic rubber
ATBN	amino-terminated butadiene-acrylonitrile
BOPP	biaxially oriented polypropylene
CPP	cast polypropylene
CPVC	chlorinated PVC
CR	polychloroprene
CTBN	carboxy-terminated butadiene-acrylonitrile
CTE	coefficient of thermal expansion
CTV	cure through volume
DGEBA	diglycidyl ether of bisphenol-A
DiCy	dicyandiamide
DIY	do-it-yourself
EB	electron beam
EGR	Exhaust Gas Recirculation engines
EMI	electromagnetic interference
EPDM	ethylene-propylene-diene terpolymer
E-SBR	emulsion SBR
ETBN	epoxy-terminated butadiene-acrylonitrile
ETDA	ethylenediaminetetraacetic acid
EVA	ethylene-vinyl acetate copolymer
EVCL	ethylene-vinyl chloride copolymer
FDA	US Food and Drug Administration
FKM	fluorinated elastomer
FRP	fibre-reinforced plastics
GDP	gross domestic product
HDI	hexamethylene diisocyanate
HDPE	high density polyethylene
HNBR	hydrogenated nitrile
IPD	isophorone diisocyanate
IR	polyisoprene
JMC	joint movement capability
JV	joint venture
LDPE	low density polyethylene
LEV	low emission vehicle standard
LLDPE	linear low density polyethylene
MDF	medium density fibreboard
MDI	methylene diphenyl diisocyanate
MDPE	medium density polyethylene
MEK	methyl ethyl ketone
MF	melamine-formaldehyde
MS	modified silicone
MUF	melamine-urea-formaldehyde
MVTR	moisture vapour transmission rate
NBR	acrylonitrile-butadiene copolymer
OEM	original equipment manufacturer
OPP	oriented polypropylene
OSB	oriented strand board
PABST	Primarily Adhesive Bonded Structure Technology
PCB	printed circuit boards
PE	polyethylene

PF	phenolic resins
PF	phenol-formaldehyde
PIB	polyisobutylene
PP	polypropylene
PSA	pressure sensitive adhesives
PTFE	polytetrafluoroethylene
PU	polyurethane
PVA	Polyvinyl acetate
PVC	polyvinyl chloride
PVDC	polyvinylidene chloride
RF	radio frequency
RHMU	reactive hot melt urethane
RPP	Resolution Performance Products
RTV	room temperature vulcanised
RTV-1	room temperature vulcanisable, one-component
RTV-2	room temperature vulcanisable, two-component
SBC	styrenic block copolymer
SBR	styrene butadiene rubber
SBS	styrene-butadiene-styrene
SGA	second generation acrylics
SIP	structural insulated panel
SIS	styrene-isoprene-styrene
SMA	surface mount adhesives
SMC	sheet moulding compound
SMD	surface mounted device
SMT	surface mounted technology
S-SBR	solution SBR
ST	silyl terminated
TDI	toluene diisocyanate
T <sub>g</sub>	glass transition temperature
THT	through-hole technology
TPO	thermoplastic polyolefins
UF	urea-formaldehyde
UHMWPE	ultra-high molecular weight polyethylene
UL	Underwriters' Laboratories
ULDPE	ultra low density polyethylene
UV	ultraviolet
VA	vinyl acetate
VA/E	vinyl acetate-ethylene
VOC	volatile organic compounds
VTBN	vinyl-terminated butadiene-acrylonitrile
X-NBR	carboxylated NBR
X-SBR	carboxylated SBR



# Rapra Market Reports

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